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THERMO-ELECTROMOTIVE FORCE, PELTIER HEAT, AND THOMSON HEAT UNDER PRESSURE.

By P. W. Bridgman.

Investigations on Light and Heat made and published with aid from the Rumford Fund.

(Continued from page 3 of cover.)

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Introduction.

The effect of pressure on the electrical resistance of a large number of metals over a considerable range of pressure and temperature (0° to 100° C, and 0 to 12000 kg/cm^2) has formed the subject of two recent papers.[1] The facts there presented suggested new points of view concerning the mechanism of electrical conduction in metals. Since, however, conductivity is only one of the electrical properties of metals, we would expect that information regarding all electrical

1 P. W. Bridgman, Proc. Amer. Acad. **52**, 571–646, 1917.
Phys. Rev. **9**, 269–289, 1917.

properties would be desirable in attempting to picture the complete electrical mechanism. I stated in the previous papers that I hoped to obtain additional measurements on thermo-electrical properties.

In this paper these thermo-electric measurements are carried out. The change in the thermo-electric properties of nearly all the metals whose electrical resistance was there measured is here given over the same range of pressure and temperature; a few only of the metals were not adapted to these measurements and could not be used. In addition, new data are given for the effect of pressure on both electrical resistance and thermo-electric properties of the alloys manganin and constantan. In most cases measurements of the thermo-electromotive force were made either on identical pieces of wire, or on pieces from the same specimen as were the resistance measurements. In the few cases where new specimens of metal had to be used, the temperature coefficient of resistance at atmospheric pressure has also been measured, in order to define the electrical character of the metal as completely as possible.

The results of this paper, unlike those of the previous paper on resistance, are almost entirely novel; the nature of the results to be expected was not known, and accordingly these effects, so far as affected by pressure, were not available for any theoretical considerations. Previous measurements on the effect of pressure on thermal e.m.f. are very few in number, and cover a very restricted range. The maximum pressure reached has been by Wagner,[2] 300 kg., over the same temperature range as that used here, 0° to 100°. Over a pressure range so small, the effect is in most cases so minute as to be on the limits of the readily measurable. Previous measurements have been almost entirely confined, of necessity, to determining the total effect of the maximum pressure and temperature. It was not possible to find at all accurately whether the effect was linear with pressure and temperature within the range employed. On a few metals Wagner made measurements of the effect of varying temperature, and found that within his limits of error the effect was linear. The effects are so much larger over the much greater pressure range of this paper that I have been able to make accurate measurements of the variation of the effect with pressure and temperature within the range. This is important, especially the variation with temperature. For it is well known that the Peltier heat is determined by the first derivative of the thermal e.m.f., and the Thomson heat by the second. Previously

2 E. Wagner, Ann. d. Phys. **27**, 955–1001, 1908.

we had only rough indications of the initial direction of variation of Peltier heat with pressure and no indication whatever as to even the sign of the change of Thomson heat. The present measurements afford fairly accurate data about the Peltier heat over the entire range of temperature and pressure, and somewhat less accurate information, but still accurate enough to give the essential features of the situation, with regard to the Thomson heat.

In one other particular these measurements have an advantage over previous ones in this field. Recent improvements in moving coil galvanometers, as well as the greater size of the effect, have made it possible for me to use this type of galvanometer, instead of some form of Thomson galvanometer. Every one knows how enormously more convenient the moving coil galvanometer is than the Thomson. It was possible to make these measurements like any others of physical routine, at all times of the day, with no disturbance from outside changes, instead of waiting for the exceptionally favorable conditions of the early morning hours, as previous observers have been forced to do.

In addition to the effect of hydrostatic pressure on thermo-electric quality, this paper contains measurements on the effect of tension. In my previous work on resistance effects, it appeared that there is a simple relation between the effects of hydrostatic pressure and tension on resistance, which had theoretical significance. I hoped for a similar state of affairs with respect to thermo-electric properties, but on looking up previous data found such discrepancies between different observers on the effect of tension, as to cast doubt on even the sign of the effect in some cases. I therefore made a fresh experimental examination with some of the metals of the pressure measurements. It appears that the discrepancies between different observers is due to the inherent nature of the effect. Results are not at all reproducible, sometimes different lengths from the same spool give effects of different sign. The situation with respect to tension is therefore quite different from that with regard to hydrostatic pressure. The effects produced by hydrostatic pressure on thermo-electric quality have a definite physical significance; reproducible results are obtainable, and different observers may agree, at least for normal metals, as is shown by the quite unexpectedly good agreement between the results of Wagner and myself over the range common to our work. But the tension effects show no such regularity, and apparently depend more on accidental incidents, such as difference in mechanical handling. In the following, little space is devoted to this aspect of the question,

therefore, but I have taken the opportunity to record at least the general nature of the results.

The plan of presentation of the paper is this: first is given the methods of measurement and computation, and then the detailed account of the effect of hydrostatic pressure on thermal e.m.f., Peltier heat, and Thomson heat; this is followed by a brief presentation of the effect of tension on thermo-electric quality; finally the results are collected for a general survey, and some theoretical deductions suggested. This work was distinctly disappointing regarding theoretical conclusions or suggestions as to mechanism. It appears from these measurements that thermo-electric properties, as we measure them, are probably a residual of different effects, sometimes working in opposite directions, and that, for the present at least, these results cannot be as suggestive as I had hoped for an electron theory of metals.

In trying to interpret these results I have been obliged to think through the general subject of thermo-electric phenomena, and have been much impressed by the confusion that reigns in this field, even respecting fundamental matters. As a preliminary to further work I have brought together a number of general considerations, which I hope may form a basis for at least consistent thought. These general considerations seem proper subject for a separate paper, and I hope to publish them elsewhere; they may, however, be read in connection with this paper if the reader should at any time find himself in doubt as to my precise position.

Apparatus and Experimental Methods.

The general method is that which naturally suggests itself for measuring an effect as small as this, and is the same as that used previously by Wagner.[2] Instead of using an ordinary thermo-couple, say of copper-constantan, subjecting the whole couple to hydrostatic pressure, and measuring the change in thermal e.m.f. at different pressures when the difference of temperature of the terminals is predetermined, the two branches of the couple are made of the same metal, the metal under examination, and one branch only is subjected to pressure. The metal under pressure behaves effectively like a different metal from that not under pressure, and we measure the thermal e.m.f. of the metal against itself in the uncompressed state. The advantage of this, of course, is that except for inhomogeneities in the wire the entire effect measured is the effect sought, instead of only a small change in a relatively large effect.

Such a couple involves both temperature and stress gradients. The stress gradient is rendered ineffective by keeping the regions in which there is such a gradient at constant temperature. Thermodynamics shows that no closed circuit of the same or different metals under different or varying stresses can possibly be the seat of an e.m.f. if the whole is at one constant temperature. If, then, all regions of

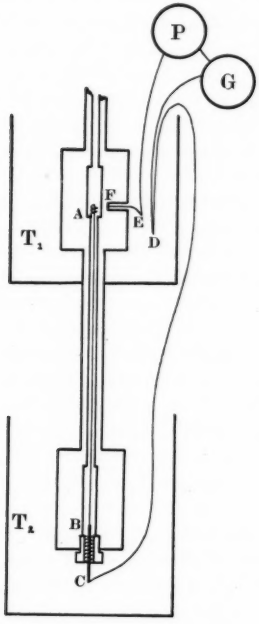

FIGURE 1. The electrical connections in place in the pressure cylinders.

varying temperature in a complete circuit are regions of no stress gradient, we are sure that stress gradients in other parts of the circuit can produce no resultant e.m.f. around the circuit.

The part of the apparatus concerned in the thermal e.m.f. measurements consists of two heavy cylinders connected by a heavy tube. The two cylinders are maintained at any required difference of tem-

perature by thermostats. Through the tube connecting the cylinders, and insulated from it, runs the wire on which measurements are to be made. This is metallically connected to the inside of the upper cylinder, but passes out through an insulating plug at the bottom of the lower cylinder. The circuit is completed outside the cylinders by a wire of the same metal, making connection through the insulating plug at the lower end, and at the upper end making a screw contact with the steel of the upper cylinder. The return wire is broken by the insertion of copper leads connecting with the galvanometer and the potentiometer for measuring the electro-motive force. The terminals of the copper leads are connected to the return wire inside a constant temperature bath so that no e.m.f. (or at least no variable e.m.f.) is introduced here. The two cylinders and the connecting pipe are filled with liquid to which pressure may be applied.

The circuit consists of the metal AB about 18″ long under a constant hydrostatic pressure, between the two ends of which there is a known temperature difference equal to the difference of temperature of the two thermostated baths; a length of nickel steel BC which forms the stem of the insulating plug, in which there is a stress gradient from the whole hydrostatic pressure inside to zero at the outer end, but in which there is no temperature gradient; a length CD about 4 ft. long of the metal under examination, running at atmospheric pressure from the temperature of the lower bath to that of the upper bath; the copper part of the circuit from D to E, entering and leaving at the same temperature; a short length, about 6 inches, of the metal under examination running from the copper at E to mechanical contact with the steel of the cylinder at F; and finally the circuit is completed through the solid steel of the cylinder between F and A, in which there is an intense stress gradient, but no temperature gradient. It is evident that the e.m.f. of this circuit is merely that of the uncompressed metal against the compressed metal between the temperatures of the two baths.

The measurements consist in finding the e.m.f. in circuits of different metals under different temperature differences and different pressures. Of course, if the inside and outside wires are precisely alike, there is no e.m.f. for any temperature difference unless there is also a pressure difference. But this ideal condition was seldom attained, as the wires were never precisely alike; the readings had to be corrected by the zero reading, which of course varied with the temperature difference.

The two cylinders were connected to the apparatus for producing pressure through a tube screwed into the upper end of the top cylinder.

This was the same apparatus as that used in much previous work,[3] and has been described so thoroughly that no further description is needed here. The pressure was measured throughout with the same coil of manganin wire as that used for the measurements of pressure coefficient of resistance. It was calibrated from time to time. The pressure part of all this work went more smoothly than ever before; the complete set of measurements on 24 different specimens was made without a single rupture, except one pinching off of the stem of an insulating plug, and with only a few leaks due to defective washers.

Various details of manipulation had to be carefully observed in order to get good results. It is well known that thermal e.m.f. is exceedingly sensitive to slight mechanical changes. For instance, the wire of an ordinary constantan thermo-couple cannot be bent without changing its constants. I was prepared, therefore, to expect very large irregularities at these high pressures, and was most pleasantly disappointed to find that, with some precautions, reliable measurements could be obtained. It is above all else necessary to avoid all permanent distortion. The viscosity of most liquids becomes so great under high pressure that permanent distortion may easily result. The connecting tube is about 18 inches long, and the hole $\frac{1}{8}$ inch diameter. When pressure is increased or decreased the entire liquid in the tube moves bodily one way or the other, because of change of volume in the liquid in the lower cylinder, and if the liquid is sufficiently viscous will carry the wire with it, and in some cases may easily break it. The magnitude of this viscous drag depends on the diameter of the wire; the smaller the diameter the larger the ratio of surface to cross section, and the larger the effect. It was desirable for this reason to use in many cases a wire larger than that on which resistance measurements were made, and I therefore prepared a number of new wires from the same samples as the old wires. Viscous drag may result either in a permanent distortion of the wire, showing itself as a permanent change of the zero reading, or it may produce an effect within the elastic limit which disappears with release of pressure. Such an elastic effect was shown by several of the smaller wires; it may be eliminated by reversing the direction of the change of pressure. The viscous effect can be reduced in most all cases to negligible proportions by using a very thin liquid to transmit pressure, changing pressure slowly, and by running pressure back and forth several times over a small range before making a reading. The liquid found suitable was petroleum ether, which had also been

3 P. W. Bridgman, Proc. Amer. Acad. **49**, 627–643, 1914.

used before in the resistance measurements partly mixed with kerosene. This was always now poured pure into the lower part of the apparatus without admixture of kerosene. The upper of the three cylinders was initially filled with a mixture of equal parts kerosene and ether. This liquid remains so thin under even the highest pressures that somewhat more trouble was found from minute leaks than ever with undiluted kerosene. The bearing surfaces of the washers must be in very good condition, otherwise leak takes place along scratches on the steel too minute to be sufficiently closed by the plastic flow of the steel at high pressures. However, all these minute leaks closed up automatically under sufficiently long duration of pressure, and never could introduce any error in the readings, which were made only after leak had disappeared. Leak merely made the manipulation somewhat more inconvenient. The use of petroleum ether made it impossible, because of its low boiling point, to make measurements at atmospheric pressure at the higher temperatures. Above 25°, therefore, the initial readings were made at pressures of 300 kg., and extrapolation made to atmospheric pressure.

The effect of viscous drag was further increased by the necessity for insulating the wire AB from the steel tube. The wire was in most cases bare, and insulation was provided by slipping over the wire short lengths ($\frac{1}{2}$ inch long) of thin glass tube. It was necessary to choose these of the best diameter. If they were too large, the viscous resistance between the glass and the wall of the steel tube was so great that all the pieces moved together bodily, and might cut off the wire at the upper end; whereas if the glass tube was too small the viscous resistance between the glass and the wire was so great that the stress on the wire was no longer truly hydrostatic. The best size for the glass was found after several trials. That the effect of viscous drag was finally successfully eliminated is shown by the fact that even for metals as soft as lead and thallium the permanent change of zero after a run to 12000 kg. was less than $1/10\,\%$ of the total effect.

The inner wire was attached to the lower insulating plug with soft solder, except in a few cases such as magnesium or aluminum, when connection was made by wrapping the joint with small copper wire and smothering over the outside with soft solder. Slight variations of resistance at the contacts evidently were of no importance, and it therefore was not necessary to take the precautions used in the resistance measurements. At the upper end, a flexible connection to allow for inequalities of compression and relative motion between the cylinder and the core of the insulating plug was made by soft

soldering the wire to a helix of copper wire, which was in turn soldered to the connecting tube. Connection between the tube and the cylinder was amply provided by the mechanical contact through the threads, which supported the entire thrust of the internal pressure. The soldered connection at the top of the wire was not made until after the bottom connection had been made and screwed into position, so that all initial strains of tension or torsion were avoided. The outer wire was protected over its entire length by a loosely fitting rubber tube, which slipped over the outer end of the insulating plug and prevented contact with the water of the bath. The connections at E and D to the copper leads to the electrical part of the apparatus were made with soft solder. The wire FE and part of the copper lead in the upper bath were also protected with rubber tubing. The two connections E and D were placed close together and tied to the outside of the upper cylinder. They were protected from direct contact with the water of the bath with a covering of felt 1 inch thick. The temperature of these junctions was therefore controlled by the large mass of the cylinder and remained constant in spite of small fluctuations in the bath liquid. The copper leads from E and D were taken from the same spool and were so homogeneous that no undesirable e.m.f. was ever introduced by this part of the circuit. The connection at F was a mechanical connection. A small hole was bored from the outer surface of the cylinder to within $\frac{1}{2}$ inch of the inner surface. Against the flat bottom of this hole a steel tube which contained the wire was forced by a nut. This wire was lead axially through the tube, and insulated from it, except at the very end, where it was soldered in place with enough soft solder to make a little mound at the bottom of the tube. When forced into place by the screw, this mound was flattened out, making at the same time good electrical contact and preventing contact between the water of the bath and the wire. This wire was brought as close as possible to the inside of the cylinder in this way in order to reduce to a minimum any disturbance arising from slow fluctuations in the temperature of the bath. Any irregularity introduced by flow of heat into the bath along the pressure tubing, either above or below, may be shown by a simple computation to be absolutely negligible; any such effect is certainly less than 10^{-6} degrees. The upper bath was the variable bath, and was controlled by a thermostat within 2 or 3 thousandths of a degree. In virtue of the precautions just described all appreciable errors due to temperature control were eliminated. In the lower bath, slow variations in temperature would be of greater effect, because of the long stem of the

insulating plug, so that it was necessary that the two ends of this stem be at exactly the same temperature. This source of error was reduced to a minimum by always using the lower bath as an ice bath. The lower tank was kept full of ice and water, well packed down, and a violent circulation of water through the ice was maintained with a stirrer. The bath was also heavily lagged. The result was completely satisfactory, but I have been impressed during this work, as well as in some other, by the absolute necessity of maintaining a violent circulation of water if complete uniformity of temperature is to be secured. An ice bath, even when continuously repacked, develops local inequalities of temperature, unless the water is stirred. Of course the conditions here were somewhat severe, because there was a constant rather large inflow of heat from the upper bath along the pressure tubing.

The electrical-measurements part of the apparatus now requires description. There were two entirely independent electrical systems involved. One was for measuring the pressure by means of the change of resistance of the manganin coil.[4] This has already been fully described. The other was to measure the thermal e.m.f. The range of e.m.f. to be measured was from a fraction of a micro volt to 0.0007 volts. The galvanometer used was of the Leeds and Northrup high sensitivity D'Arsonval type. It was specially constructed to my specifications; was critically damped on 5 ohms external resistance, with a period of 7.8 seconds and a sensitivity of 1.5 cm. at 1 m. distance for 10^{-6} volts. Its internal resistance was 12 ohms, so that as long as the resistance of the external circuit remained under 5 ohms its performance was sufficiently constant. The wires used were almost always large enough to meet this requirement. In use the galvanometer was set up at 3 m. distance and gave 4.5 cm. deflection for 10^{-6} volts. The method used was a double throw null method, and the steadiness was great enough so that 0.1 mm. could be easily obtained. Readings could therefore be made to 10^{-9} volts. I have to express special obligations to the Leeds and Northrup Co. for this instrument. At the time, certain of the materials necessary for the construction of a new instrument were not to be obtained in the market, and they were so kind as to take from their own shops one of their experimental instruments and rebuild it to specifications.

The method of measuring e.m.f. was a potentiometer method, in which the unknown e.m.f. is tapped off around a fixed resistance, and

4 P. W. Bridgman, Proc. Amer. Acad. **47**, 321–343, 1911.

the current in the potentiometer circuit varied by means of a suitable resistance until balance is obtained. This has the advantage over the ordinary slide wire form of avoiding all possible e.m.f's. at the sliding junctions. In order to provide the very small e.m.f's. required, the known source of e.m.f. was stepped down twice. The comparison cell was a battery of ten acid Weston cells connected in parallel. The advantage of the acid cell is that its e.m.f. does not fluctuate, even when a comparatively large current is drawn. This was most kindly loaned to me by Professor H. N. Davis, by whom it had been personally constructed. I am also indebted to him for a number of the other pieces of standard apparatus used. The e.m.f. of the acid cell varies somewhat with the external resistance; it was measured by standard potentiometer methods against a standard Weston cell for external resistances from 1000 to 10000 ohms. The e.m.f. at the terminals varied under these conditions from 1.0410 to 1.0425 volts. This was measured several times in the course of the work, and the voltage under any given external resistance remained constant within 1/100%. The temperature effect was negligible for temperature fluctuations within the range of this work.

The working cell was connected through a reversing switch with a 10,000 and a 10 ohm. coil in series. The 10 ohm coil was tapped by a second circuit containing a variable Leeds and Northrup decade box reading to 10,000 ohms, and guaranteed to 1/10%, and three other coils, of seasoned copper, of 10, 1 and 0.1 ohm. According to its magnitude, the e.m.f. in the pressure circuit could be tapped across either the 10, 1, or 0.1 ohm coil. Readings were made by a null method by the method of reversals. Reversing switches in the pressure circuit, but not in the galvanometer circuit, and in the second stage of the potentiometer circuit allowed the reversal of both the e.m.f. being measured and the balancing e.m.f. The decade box was set until no throw was obtained on reversing both these circuits. The range covered with the apparatus set up as above was from approximately 10^{-8} volts, with 1000 ohms in the decade box and 0.1 ohm tapped, to 10^{-5} volts with 1000 in the decade box and 10 ohms tapped. For larger voltages the working cell could be directly connected with the potentiometer circuit, increasing the range in this way from 10^{-5} to 10^{-2} volts, still with never less than 1000 ohms in series with the working cell. E.m.f's. less than 10^{-8} volts were read by the deflection of the galvanometer without attempting to balance. Of course the e.m.f's. corresponding to the stated resistances are not exactly those given, but there are slight corrections. The corrections

as a function of the resistance may be readily calculated by Kirchhoff's laws, and such corrections were applied in all the computations.

It is not worth while to go into greater detail about this electrical installation, except to say that in designing it and setting it up I profited much by suggestions in various papers of White.[5] All leads were of copper from the same spool. All connections were either soldered (with pitch) or were the clothes pin type of spring clip, with the in-leading wire thermally protected by wrapping with copper strip, as advocated by White. All switches, both single throw and reversing, were of the jack knife type, and of all-copper construction. All the connections and switches, except the pressure connections already described and the connections to the galvanometer binding posts, were inclosed in a single covered box, to secure temperature equality, and all switches were operated through the sides of the box with rods. The reversing switches were so connected together with a sliding rod as to be operated by a single push or pull, and were so related in phase than an unbalanced e.m.f. was never thrown on the galvanometer at any stage of the reversal. The copper resistance coils of 10, 1, and 0.1 ohms were immersed in an oil bath of Bureau of Standards resistance oil inside the same box as that housing the switches, and the oil was stirred and the temperature read with a thermometer reaching through the walls of the box after every reading of e.m.f. The resistance of the copper coils was measured at 22° on a Carey Foster bridge against coils calibrated at the Bureau of Standards. The temperature coefficient was not measured, but was assumed to be 0.00382 at 22°. This corresponds to copper of conductivity 98%. If the copper were actually anywhere from 96% to 100% conductivity, which is greater than the variation met with in commercial copper, the error so introduced would remain less than 0.1% over a temperature range of 10°, which was the maximum variation in room temperature during this work.

In addition to all these, several coils not already mentioned were introduced either in parallel or in series with the galvanometer so that its sensitiveness could be appropriately varied.

The galvanometer itself was protected with a shield of heavy sheet iron heavily covered on the outside with cotton. Internal thermal e.m.f. in the galvanometer was never entirely absent, rising sometimes to as much as $\frac{1}{3} \times 10^{-6}$ volts, but the method of measurement, reversing

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5 W. P. White, Jour. Amer. Chem. Soc. **36**, 1856–1868, 1868–1885, 2011–2020, 2292–2313, 2313–2333, 1914.

the other circuits but not the galvanometer circuit, eliminated this as a source of error. An eliminating switch about the 0.1, 1, and 10 ohm coils, as described by White, showed that there were no parasitic e.m.f's. in this part of the circuit. The construction of the rest of the circuits assures that any other parasites, except in the pressure part, are overwhelmed and masked by the applied e.m.f., and parasites in the pressure part, provided they stay constant, are eliminated by the zero correction. All switches and the galvanometer were further protected by a leakage shield, as advocated by White. The whole apparatus was surprisingly satisfactory in its performance, and except with some of the more inhomogeneous metals the steadiness was such that even over the maximum temperature range individual readings could be made to the limit of sensitiveness, about 10^{-9} volts.

The accuracy of the readings was of course not usually as high as 10^{-9} volts, but varied greatly for the different metals; the details will be given later. In general, the precautions necessary to ensure reproducible results were to previously season the metal by several preliminary applications of pressure and to change pressure slowly, in order to avoid viscosity effects from the transmitting medium. Most of the metals showed no hysteresis, and the pressure measurements might have been made in any order, but they were, as a matter of fact, nearly all made alternately with rising and falling pressure.

Measurements on a single metal consisted of readings at four different temperatures of the variable bath (25°, 50°, 75°, and 95°) and seven different pressures (0, 2000, 4000, 6000, 8000, 10000, and 12000 kg./cm.^{2}). The procedure was usually as follows. The apparatus was set up and seasoned by several preliminary applications of pressure to the maximum at room temperature. The lower bath was then filled with ice and the upper bath adjusted at 25°. E.m.f. measurements were then made at 0, 4000, 8000, 12000, 10000, 6000, 2000, and 0 kg. This might occupy two hours. The time required for dissipation of heat of compression after every change of pressure was cut down by secondary variations of pressure, as has already been described in previous papers.[6] The upper bath was then changed to 50°, the lower one still being packed with ice, and e.m.f. measurements were made at the same pressures as before. This was repeated at 75° and 95°. The temperature of the bath was read on a Tonnelot thermometer calibrated at the Paris Bureau of Weights and Measures.

[6] P. W. Bridgman, Proc. Amer. Acad. **49**, 14, 1913.

In addition to the pressure measurements, the thermal e.m.f. of each of the specimens was found at atmospheric pressure against lead. The same potentiometer was used as for the pressure measurements, and no special comment is necessary. One terminal of the couple was kept in an ice bath; the other was placed successively in baths at 25°, 50°, 75°, and 95°. Twelve couples were made up and measured simultaneously. As a matter of fact, the readings were actually made against copper; the e.m.f. against lead was obtained by a subtraction. The e.m.f. against temperature of each of these couples could be represented within the limits of error by a power series in t (three terms were always sufficient). These formulas are given in the following as a further means of identifying the metal. By one and two differentiations the Peltier heat against lead and the Thomson heat at atmospheric pressure may be at once obtained. These are also listed in the following. A positive e.m.f. means that the positive current flows from lead to the metal at the hot junction.

Methods of Computation.

The thermal e.m.f. in the pressure circuit was first computed for each reading, applying all corrections, including temperature corrections. The points were then plotted on a large scale, thermal e.m.f. against pressure, and smooth curves drawn through the points at each temperature. In this way four smooth curves were obtained for each substance, or really five curves, because the curve corresponding to 0° coincides with the pressure axis. From this bundle of smooth curves the thermal e.m.f. could be read as a function of temperature at constant pressure. The curves were in this way replotted, giving thermal e.m.f. against temperature at constant pressure. Six pressures were chosen, 2000, 4000, 6000, 8000, 10000, and 12000, giving six smooth curves of thermal e.m.f. as functions of temperature. The smoothing so far was done graphically. A further smoothing was next performed by calculation. The ordinates were read from the six smooth curves at intervals of 10°, and the differences of successive ordinates computed. The curves were now further adjusted so that the successive differences should lie on a smooth curve when plotted on a scale 10 times as large as the original curve. This second adjustment was of course performed so as not to produce any changes greater than the uncertainties in the original plot. The smoothed first differences, obtained in this way, are equal, without appreciable

error, to ten times the slope of the curves at the mid-temperatures of the 10° intervals. This gives immediately, therefore, $\frac{dE}{dt}$. Multiplying this by the absolute temperature gives, by a well known formula, the Peltier heat at the hot junction. The Peltier heat was so calculated and is tabulated in the following. From the tabulation of first differences the second differences were next found by successive subtractions. These were plotted and smoothed graphically, giving at once $\frac{d^2E}{dt^2}$. This, multiplied by absolute temperature, gives the difference of the Thomson heat in the compressed and the uncompressed metal at the temperature in question. This is also tabulated in the following. Perhaps to give the results as accurately as possible an additional smoothing for pressure should have been introduced. But this seemed to me an additional refinement not justified by the reproducibility of the results.

The convention adopted for the sign of the effect requires explanation. In the following, the thermal e.m.f. of the circuit is called positive if at the hot junction the current flows from uncompressed to compressed metal. The Peltier heat is considered positive if heat is absorbed by the positive current from the surroundings on flowing from uncompressed to compressed metal. A positive $\frac{d^2E}{dt^2}$ means a larger Thomson heat in the compressed than the uncompressed metal, and the Thomson heat is itself considered positive if heat is absorbed by the positive current in flowing from cold to hot metal. In other words, a positive Thomson heat corresponds to a positive specific heat of the positive current, or a negative specific heat of the current of electrons. The opposite convention is sometimes used for the Thomson heat.

The detailed presentation of data follows. The order of arrangement of the metals is the same as that in the previous paper on resistance. Four metals used there could not be used in this investigation. These were: Indium and Tantalum, of which I did not have a large enough supply, and Antimony and Tellurium, which are so brittle as to make hopeless any manipulation of continuous pieces four feet long. In addition to the metals of the resistance paper, two alloys, manganin and constantan, are included at the end of the list. The pressure effect on the resistance as well as on the thermal e.m.f. has been measured.

The data are chiefly given by tables and diagrams. There are in

general three tables for each metal. The first table shows the total e.m.f. of a circuit composed of uncompressed and compressed metal. The lower junction is always at 0°; the entries in the table show the e.m.f. for different temperatures of the upper junction, and for different pressures of the compressed branch. The temperature interval of this table is 10°, and the pressure interval 2000 kg. The e.m.f. corresponding to 0° is, of course, zero for all pressures. The second table gives the Peltier heat absorbed by unit quantity of positive electricity in passing from uncompressed metal to metal compressed to the pressure in the table, both uncompressed and compressed metal being at the temperature indicated in the table. The temperature interval is 20°, and the pressure interval 2000 kg. in the second table. The third table shows how much greater the Thomson heat is in metal compressed to the pressure of the table than in uncompressed metal, both uncompressed and compressed metal being at the temperature indicated in the table. The temperature interval of the third table is also 20°, and the pressure interval 2000 kg. The diagrams give graphically the results of the tables, plotted at constant pressures against temperature. The scale of the diagrams of Peltier heat and Thomson heat is half that of the e.m.f. diagrams. The smaller scale for the two heats has been chosen because of their smaller accuracy. The corresponding tables for all metals are given in the same sized units, so as to facilitate direct comparison.

Detailed Data.

Tin. This was Kahlbaum's "K" tin, from the same small ingot as that whose resistance under pressure was measured, but not the identical piece of wire. It was made by extrusion at 100° into wire 0.02 inches in diameter, considerably larger than the resistance wire, and was annealed in an electric furnace to 120° for several hours. It was not subjected to a preliminary pressure seasoning for the runs; this is unnecessary for soft metals.

Tin was one of the most unsatisfactory metals measured, because of the minuteness and irregularity of the effect. Tin is known to form other allotropic modifications below 20°, the reaction usually not running because of internal viscosity. During the experiment, therefore, the lower end of the wire was probably always in the metastable region, and the readings themselves gave evidence of internal instability. The readings were never steady, but continually flickered

by small amounts which might rise to as much as 0.04×10^{-6} volts at the highest temperature. Furthermore, all runs showed considerable hysteresis, which of course is characteristic of a substance not in perfect equilibrium. The zero was usually recovered with fair accuracy; at 98° the zero error was hardly 1% of the total effect, but at 75° there was some sort of progressive change during the run, which of course produced the largest effect at zero. The readings at 75° failed by about 30% to fall on a smooth curve with those at other temperatures, and the 75° points were accordingly disregarded in drawing the curves.

In spite of the irregularities, the uncertainties never became great

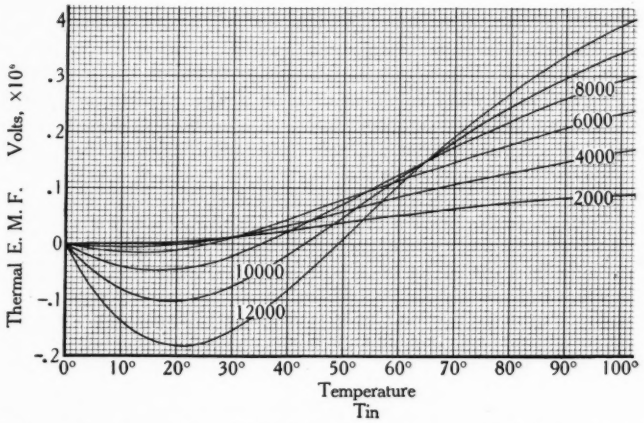

FIGURE 2. Tin. Thermal E. M. F. of a couple composed of one branch of uncompressed metal, the other branch compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

enough to obscure the essential character of the results, which are most curious. The results are shown in Figure 2, and Table I, in which e.m.f. at constant pressure is plotted against temperature. The effect is small, rising at the most to 0.4×10^{-6} volts, and reverses in sign with temperature. At 12000 kg. the e.m.f. passes through a negative maximum of 0.18×10^{-6} at about 25°, and then reverses sign, rising to 0.4×10^{-6} volts at 100°. Or if the results are plotted as a function of pressure at different constant temperatures (which

TABLE I.

TIN.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+.001	−.004	−.014	−.041	−.083	−.136
20	+.003	.000	−.010	−.045	−.103	−.182
30	.012	+.012	+.011	−.020	−.075	−.154
40	.024	+.033	+.042	+.021	−.019	−.081
50	.038	.058	.078	+.070	+.048	+.010
60	.052	.083	.111	.122	+.117	+.103
70	.064	.106	.146	.172	.183	.191
80	.074	.127	.176	.218	.243	.269
90	.082	.147	.206	.258	.296	.335
100	.087	.165	.232	.292	.341	.390

is the way in which they were obtained experimentally) they are equally curious. At 25°, the effect is initially positive, passing through a very flat maximum of about 0.005×10^{-6} volts at 2500 kg., and from here on becomes rapidly negative, reaching -0.185×10^{-6} at 12000 kg. This curve is concave downwards. The approximate effect of higher temperatures is merely to rotate this curve bodily, without distortion, anticlockwise about the origin. At 50° the effect is throughout positive, the curvature displaying itself as a maximum near 7000 kg., and at 75° and 100° the rotation has become great enough to obliterate the maximum.

The Peltier and Thomson heats deduced from these measurements are shown in Figure 3 and Table II. Of course when the fundamental data are so irregular there must be much uncertainty in the derivatives, but I believe that the essential features of the situation, with respect to changes of sign etc., are correctly given, and that the numerical values of the Thomson heat are correct to within perhaps 50%. Both Peltier and Thomson heats change sign in the range. At low temperatures the effect of all pressures is to give a negative Peltier heat; that is, heat is absorbed by the positive current in flowing across the junction from compressed to uncompressed metal, but at

higher temperatures, at all pressures, the Peltier heat becomes positive, passes through a maximum, and decreases again. The Thomson heat, on the other hand, is initially positive for low temperatures, but becomes negative at higher temperatures.

Tin was one of the metals measured by Wagner.[2] He made only one measurement, at 300 kg. and 100°, and found for the effect -0.95×10^{-12} volts per degree per kg. The measurements above

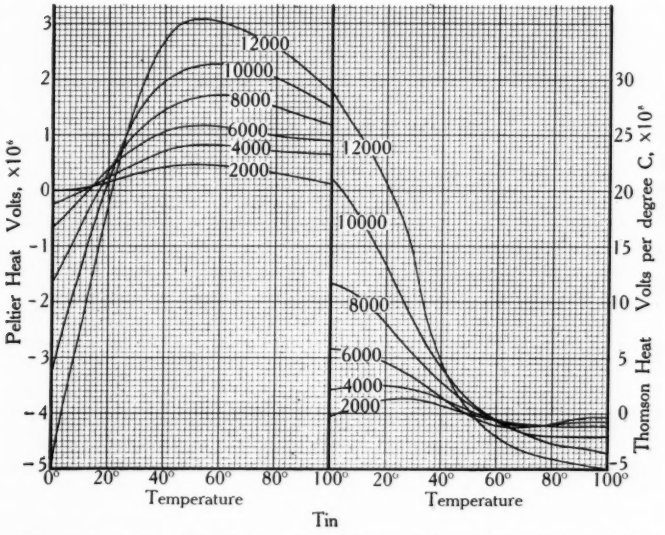

FIGURE 3. Tin. On the left, the heat absorbed by unit quantity of electricity on flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

make the effect positive at all pressures for a temperature range of 100°, and would indicate, if interpolation is justifiable, $+ 0.43 \times 10^{-12}$ volts per degree per kg. Wagner's one reading allowed him to form no idea of the complicated state of affairs for this metal. There can be no comparison between his results and mine, because it will be shown later in the case of Al and Fe, which also show reversals in sign like Sn, that small variations in the purity of the metal, or the

TABLE II.

TIN.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	0.	−.25	− .66	−1.64	−3.28	−4.92
20	+.15	+.23	+ .38	+ .32	+ .15	− .23
40	+.41	+.72	+1.06	+1.44	+1.94	+2.68
60	.43	.80	1.13	1.73	2.27	+3.03
80	.30	.71	.99	1.52	2.01	2.54
100	.11	.65	.90	1.19	1.49	1.75

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	− .3	+2.2	+5.9	+11.7	+21.0	+28.9
20	+1.3	+2.5	+4.4	+ 8.2	+13.2	+20.3
40	+ .6	+1.4	+1.6	+ 3.0	+ 4.4	+ 6.6
60	− .5	− .5	−1.0	− .7	− .5	− 2.0
80	−1.1	− .7	− .9	− 1.9	− 2.6	− 4.1
100	−1.1	− .4	− .7	− 2.0	− 3.5	− 5.0

mechanical treatment, although they leave the general character of the results unaltered, may nevertheless produce large changes in the numerical values. For instance, a slight shift in the position of the flat maximum would produce changes even of sign in the neighborhood of 500 kg.

The thermal e.m.f. of tin was measured at atmospheric pressure against lead between 0° and 100°. Over this range its thermal e.m.f. is given approximately by the formula:

$$E = (0.230\,t - 0.00067\,t^2) \times 10^{-6} \text{ volts.}$$

The Peltier heat against lead is

$$P = (0.230 - 0.00134\,t)\,(t + 273) \times 10^{-6} \text{ volts,}$$

and the Thomson heat is

$$\sigma = -0.00134\,(t + 273) \times 10^{-6} \text{ volts/°C.}$$

This assumes the Thomson heat of lead to be zero. A positive e.m.f. means that the current flows from lead to tin at the hot junction.

Thallium. A different specimen from that of the resistance measurements had to be used, the former piece having become very badly oxidized. A fresh lot was obtained from the United States Smelting Company. As provided by them it contained considerable impurity of lead and cadmium. I purified it by electrolysis, by well known methods. It was dissolved in excess c.p. H_2SO_4 and electrolyzed from dilute aqueous solution onto a copper cathode with platinum anode. The deposit is in the form of trees. These were repeatedly washed in pure water, dried in a paraffine bath at 200° in a stream of H_2, and finally melted in a glass tube in a stream of H_2. The H_2, however, was not perfectly pure, and a thin film of the yellow oxide formed on the surface of the metal during melting. This was scraped off, and the ingot formed into a wire by cold extrusion to 0.028 inch diameter. The wire was kept under pure water while waiting for use, which effectively prevented tarnishing. The outer wire was shellaced immediately before assembling. There was no such trouble from oxidation as that experienced during the resistance measurements.

The purity of this sample was not so high as that of the previous one, as shown by its temperature coefficient of resistance. The average coefficient between 0° and 100° was 0.00475, which is considerably less than that of the former sample, 0.00518. The several crystallizations in the form of various salts of the previous sample doubtless accounts for its higher purity. The relation between

temperature and resistance of this new sample was sensibly linear within the range 0° to 100°.

The thermo-electric behavior of a thallium-lead couple at atmos-

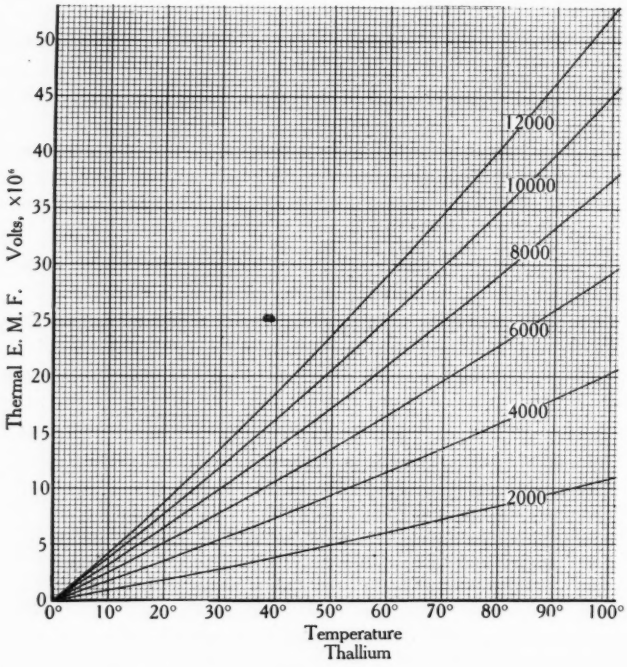

FIGURE 4. Thallium. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

pheric pressure is represented within the limits of measurement by the formulas

$$E = (1.659\,t - 0.00134\,t^2 - 0.0000056\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (1.659 - 0.00268\,t - 0.0000168\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (-0.00268 - 0.0000336\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The pressure measurements were very satisfactory. The effect is large and positive, equilibrium was quickly reached, the readings

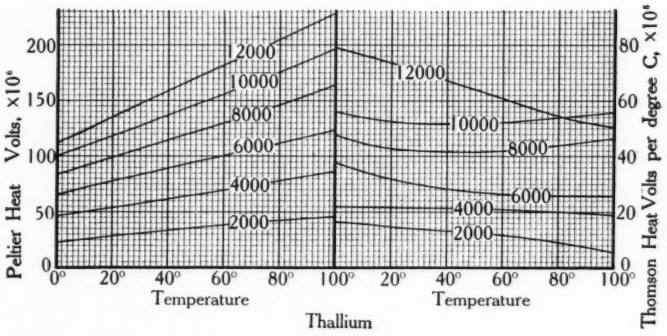

FIGURE 5. Thallium. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE III.

THALLIUM.

Thermo-electromotive Force, volts × 10^6.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+.88	+1.74	+2.47	+3.14	+3.78	+4.26
20	1.81	3.55	5.07	6.44	7.72	8.78
30	2.80	5.43	7.78	9.88	11.84	13.53
40	3.84	7.37	10.59	13.46	16.13	18.53
50	4.93	9.38	13.49	17.17	20.58	23.75
60	6.07	11.45	16.48	21.01	25.19	29.15
70	7.24	13.57	19.55	24.97	29.96	34.73
80	8.43	15.75	22.70	29.08	34.89	40.49
90	9.64	17.99	25.92	33.29	39.97	46.40
100	10.87	20.29	29.21	37.63	45.20	52.46

TABLE IV.

Thallium.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+23.	+46.	+66.	+83.	+100.	+112.
20	28.	54.	78.	99.	118.	136.
40	33.	62.	89.	114.	137.	160.
60	38.	69.	101.	130.	156.	183.
80	42.	78.	112.	147.	177.	206.
100	46.	87.	124.	164.	197.	229.

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+16.	+22.	+38.	+48.	+56.	+79.
20	15.	22.	32.	42.	53.	73.
40	12.	20.	28.	42.	52.	67.
60	12.	20.	27.	41.	52.	60.
80	9.	19.	26.	44.	55.	55.
100	6.	19.	26.	47.	56.	50.

were perfectly steady, and the permanent change of zero was almost imperceptible. The maximum departure of any point from a smooth curve was 0.4% of the total effect. It was very gratifying that this soft substance showed no permanent zero change, since permanent distortions must very easily be introduced into it.

The numerical results are shown in Tables III and IV, and Figures 4 and 5. The e.m.f. is positive and increases regularly with pressure and temperature; the Peltier heat between compressed and uncompressed metal is also positive and increases with pressure and temperature, and the Thomson heat increases with pressure, except at the maximum temperature and pressure, but decreases regularly with rising temperature.

There are no previous measurements whatever on this substance for comparison.

Cadmium. This was a piece of new wire 0.02 inch diameter, from the same original piece as the resistance wire. It was extruded at a temperature of 180°, and seasoned after extrusion by several hours at 120° in an electric oven.

The thermo-electric behavior at atmospheric pressure against lead may be represented by the formulas:

$$E = (12.002\,t + 0.1619\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (12.002 + 0.3238\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = 0.3238(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The pressure effect is not regular, and the readings were never steady, indicating an incomplete state of internal equilibrium. The material was seasoned by two preliminary applications of 12000 at room temperature, and five runs were made, at 25°, 50°, 75°, 95° and 25° again. There was much hysteresis; this was larger at the higher temperatures, and amounted at the maximum to 5% of the total effect. The run at 25° was repeated in order to find whether the hysteresis would disappear by accommodation after several runs at different temperatures, but it did not change. The first run at 25° almost exactly repeated itself, hysteresis and all. Wagner found similar effects over so low a range as 300 kg.; he found an abnormally long time required to reach equilibrium and a hysteresis which never disappeared, no matter how long he waited.

It will be recalled that Cd is one of the metals for which Cohen [7] claims different allotropic forms. The evidence of this paper corro-

7 E. Cohen and W. D. Helderman, Proc. Amster. Acad. **17**, 1050–1054, 1915.

borates the theory that Cd may be in a state of unstable internal equilibrium, or at any rate of internal equilibrium which is very slowly readjusted after any change of external conditions. The measurements of the previous paper did not suggest any such state of affairs, but this need not be surprising, because it is known that thermo-

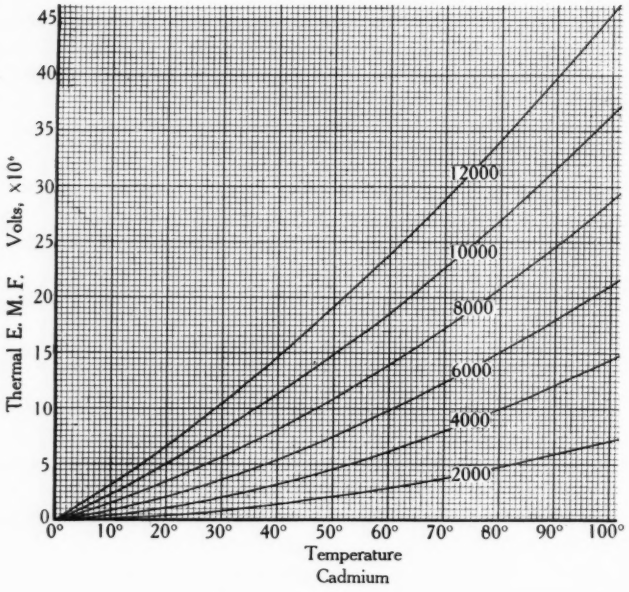

FIGURE 6. Cadmium. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.^{2} indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

electric quality is much more sensitive to slight changes than resistance. At the same time, it does not seem to me that unstable internal equilibrium necessarily points to polymorphism as an explanation. I have already discussed this matter in some detail in another paper.[8] With regard to the bearing of these particular measurements on the

[8] P. W. Bridgman, Proc. Amer. Acad. **52**, 636, 1917.

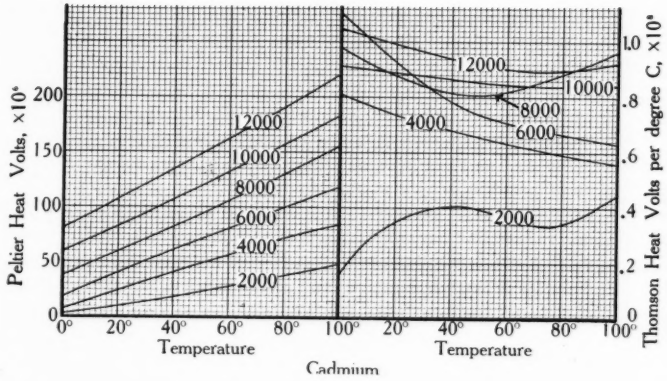

FIGURE 7. Cadmium. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE V.

CADMIUM.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+0.14	+0.42	+0.88	+1.54	+2.36	+3.16
20	0.42	1.10	2.10	3.46	5.04	6.68
30	0.84	2.06	3.64	5.70	8.04	10.54
40	1.38	3.22	5.48	8.20	11.34	14.72
50	2.04	4.62	7.56	10.96	14.82	19.18
60	2.82	6.22	9.88	13.98	18.66	23.92
70	3.72	8.02	12.42	17.28	22.76	28.92
80	4.74	9.98	15.14	20.84	27.10	34.20
90	5.88	12.10	18.06	24.66	31.70	39.74
100	7.12	14.38	21.16	28.74	36.52	45.56

TABLE VI.

Cadmium.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+3.8	+7.6	+18.6	+38.3	+60.1	+81.3
20	10.0	24.3	41.0	60.7	83.1	108.
40	18.8	40.1	61.6	82.3	107.	135.
60	28.0	56.7	80.7	105.	132.	162.
80	38.1	72.0	99.8	130.	157.	191.
100	48.5	83.2	118.	156.	183.	221.

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+16.	+82.	+109.	+98.	+91.	+105.
20	35.	73.	94.	88.	89.	99.
40	41.	69.	78.	81.	87.	94.
60	37.	63.	70.	83.	84.	90.
80	35.	60.	67.	88.	84.	90.
100	45.	56.	63.	97.	84.	93.

question, it is to be noticed that the effects were found at all temperatures of the range, increasing at the higher temperature. If the effect were due to a polymorphic transition, we would expect to find it above a definite temperature only. Cohen located the transition temperature at about 67°.

The mean curves of thermal e.m.f., that is the curves through the mean of the points with ascending and descending pressure, disregarding hysteresis, when plotted against pressure at constant temperature, are somewhat unusual in that they are concave upward, the proportional effect of a given increment of pressure thus becoming greater at higher pressures. This is not what one would expect, and is the reverse of the behavior of most metals.

The uncertainty introduced by hysteresis was so large that rather large readjustments were necessary in order to obtain smooth curves when the curves of thermal e.m.f. at constant pressure, plotted against temperature, were read from those at constant temperature against pressure. The greatest readjustment necessary was at 8000 kg. and 75°, where it was 4% of the total effect. The probable error of these readjusted curves, computing by the mean square formula from the departure of the individual points, was 0.34% of the maximum effect.

The numerical results are shown in Figures 6 and 7 and Tables V and VI. The thermal e.m.f. is large and positive, rising with pressure and temperature somewhat more steeply than normal; the Peltier heat is positive and rises with temperature and pressure, the Thomson heat is positive, and rises with temperature at the low pressures, but falls at the high pressures.

The value found by Wagner for 0° to 100° to 300 kg. was $+ 36.3 \times 10^{-12}$ volts per degree per kg., against 35.6×10^{-12} above. The agreement is much better than could be expected in view of the large hysteresis.

Lead. This was Kahlbaum's "K" lead, freshly extruded into wire 0.0288 inch diameter. It would have been desirable if I could have used the same excessively pure lead from Professor Richard's laboratory that was used for the resistance measurements, but no more was available, and the wire of the resistance measurements was too fine for this. However, this "K" lead is exceedingly pure, its temperature coefficient having been found to be only 0.2% lower than that of the purest, and it is doubtless as good as the inherently less accuracy of this work justifies.

This lead is used as the standard in this paper against which the

thermal e.m.f. of the other metals is given. Experimentally, the comparisons were all made against pieces of copper, cut from the same spool, and the figures given were obtained by subtraction. It is assumed here, from the work of previous observers, that the Thomson heat of this lead was zero; no direct examination of this question was made for these experiments, as it would have required extensive measurements with special apparatus.

As a preliminary to the pressure measurements, one previous application of 12000 kg. was made at room temperature to season.

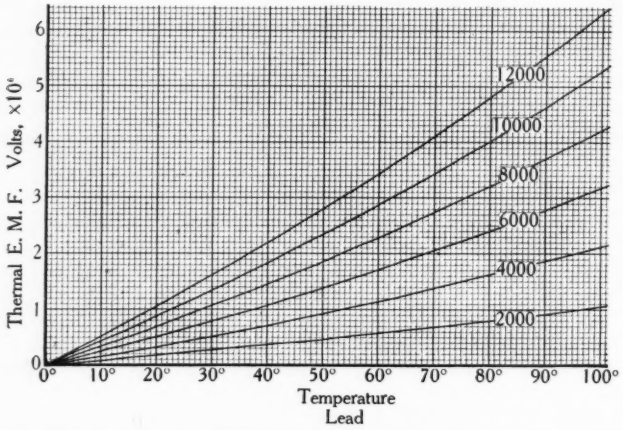

FIGURE 8. Lead. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

The pressure measurements were very satisfactory, being much like those on Thallium, although not quite so regular. The maximum effect, which is positive, is 6×10^{-6} volts against 50×10^{-6} volts for Tl. This doubtless accounts for the somewhat greater proportional irregularity. The observed e.m.f's. are sensibly linear against pressure at constant temperature. Such linearity is surprising in so soft a metal as lead. The resistance curves against pressure were distinctly not linear. There was no appreciable change of zero at any temperature, which again is most gratifying for so soft a metal.

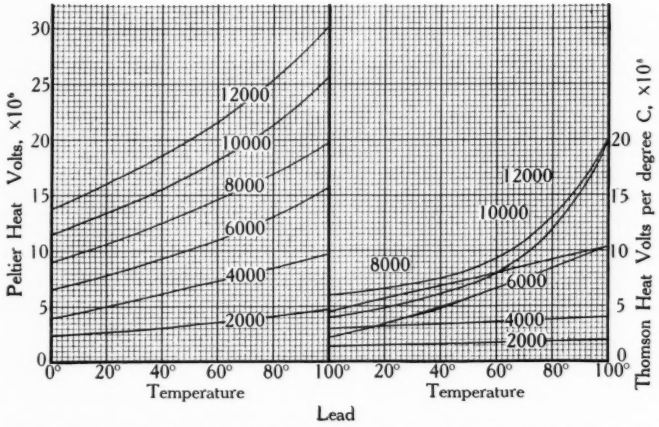

FIGURE 9. Lead. On the left, the heat absorbed by unit quantity of electricity on flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE VII.

LEAD.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²*					
	2000	4000	6000	8000	10000	12000
10°	+.08	+.15	+.25	+.34	+.43	+.52
20	.17	.32	.51	.69	.88	1.06
30	.26	.51	.79	1.06	1.35	1.62
40	.36	.71	1.08	1.45	1.84	2.20
50	.46	.92	1.39	1.86	2.35	2.81
60	.57	1.14	1.71	2.29	2.88	3.44
70	.68	1.37	2.05	2.74	3.44	4.11
80	.80	1.61	2.41	3.21	4.02	4.81
90	.92	1.86	2.79	3.70	4.64	5.55
100	1.05	2.12	3.19	4.21	5.30	6.33

TABLE VIII.

LEAD.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+2.4	+4.0	+6.6	+9.0	+11.5	+13.8
20	2.7	5.0	7.8	10.6	13.4	16.0
40	3.0	6.2	9.3	12.5	15.5	18.6
60	3.6	7.3	11.0	14.6	18.1	21.6
80	4.1	8.5	13.0	16.9	21.3	25.4
100	4.7	9.7	15.7	19.7	25.7	30.2

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+1.4	+3.0	+2.2	+4.6	+4.1	+6.0
20	1.5	3.2	3.5	5.9	4.7	6.7
40	1.6	3.4	5.0	6.9	6.3	7.5
60	1.7	3.7	6.7	8.0	8.0	9.3
80	1.8	3.9	8.5	9.2	12.0	13.1
100	1.9	4.1	10.4	10.4	20.1	20.1

According to Cohen,[9] lead also is in unstable internal equilibrium, and has allotropic modifications. No evidence whatever of anything of this kind was found above. If there had been, it should certainly have manifested itself as a change of zero. The maximum departure of any single observed point from linearity was 1.7% of the maximum effect, and the average numerical departure of all the observed points was 0.25%. Since no readjustment whatever was necessary in passing from the curves at constant temperature to those at constant pressure, the results may be accepted with considerable confidence.

The numerical results are shown in Tables VII and VIII and Figures 8 and 9. The thermal e.m.f. rises regularly with pressure and temperature, as do also the Peltier heat and the Thomson heat. All three of these are positive. The fact that there is an appreciable Thomson heat between the compressed and the uncompressed metal has an interesting bearing on the question whether there is a Thomson heat at atmospheric pressure. It is a matter of rather general experience that zero, or atmospheric, pressure, is no preferred pressure, but the properties of a substance change without discontinuity on going from negative to positive pressure. This is in accord with a point of view, fruitful in many situations, that a substance at atmospheric pressure is actually under a high internal pressure, and that changes in external pressure produce the same effect as proportionally small changes in total pressure (internal plus external). The fact, therefore, that compressed lead has a Thomson heat against uncompressed lead makes it probable that the Thomson heat of uncompressed lead is not rigorously and exactly zero but is merely too small to be measured conveniently.

Wagner is the only previous observer on lead; he gives $+ 5.6 \times 10^{-12}$ volts per degree per kg. for 0° to 100° and to 300 kg. The results above for the same range would be interpolated as $+ 5.2 \times 10^{-12}$; the agreement is satisfactory.

Zinc. This was Kahlbaum's "K" grade, from the same rod as the resistance specimen, but it was not the identical piece of wire. It was extruded to 0.020 inch diameter at a temperature of 330°, and was annealed in an electric oven for several hours at 120°.

At atmospheric pressure its thermo-electric behavior against lead is given by the formulas:

$$E = (3.047\,t - 0.00495\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (3.047 - 0.0099\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = -0.0099(t + 273) \times 10^{-6} \text{ volts/°C}.$$

9 E. Cohen and W. D. Helderman, Proc. Amst. Acad **17**, 822–828, 1914.

The behavior under pressure is in many respects like that of cadmium. Zinc evidently is in a state of unstable internal equilibrium as shown by unsteadiness and irregularity of reading, and hysteresis. The hysteresis was not as marked as that of cadmium, however, and the permanent changes of zero were comparatively small, rising at the maximum to 1.2% of the total effect. Five runs were made,

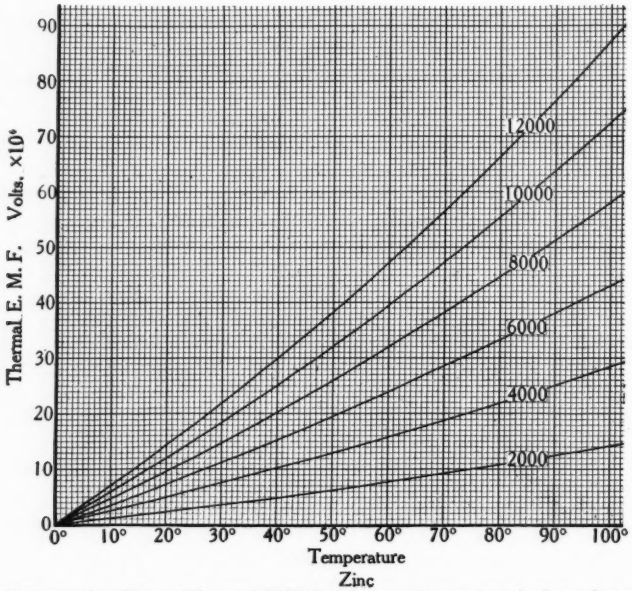

FIGURE 10. Zinc. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

at 25°, 50°, 75°, 95°, and 25° again. The last run at 25° was made to find whether any permanent change had been produced by the many changes of pressure and temperature, but there was none, the last run at 25° giving the same average deflection and also the same hysteresis as the first run. In order to reduce to a minimum uncertainties from changing internal equilibrium, two applications of the maximum

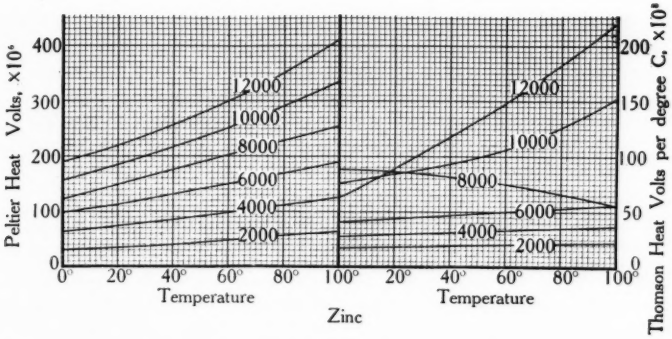

FIGURE 11. Zinc. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE IX.

ZINC.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+1.1	+2.4	+3.6	+4.7	+5.9	+7.1
20	2.3	4.9	7.3	9.6	12.0	14.4
30	3.5	7.5	11.2	14.8	18.4	22.0
40	4.8	10.2	15.3	20.3	25.1	30.1
50	6.2	13.0	19.6	26.1	32.2	38.5
60	7.8	15.9	24.0	32.1	39.6	47.4
70	9.3	18.9	28.6	38.3	47.3	56.7
80	10.8	22.0	33.3	44.7	55.3	66.4
90	12.4	25.2	38.1	51.3	63.7	76.6
100	14.1	28.5	43.0	58.1	72.5	87.4

TABLE X.

Zinc.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+30.	+64.	+98.	+123.	+155.	+190.
20	35.	75.	110.	149.	185.	218.
40	41.	86.	131.	176.	216.	257.
60	48.	98.	150.	203.	252.	300.
80	56.	111.	169.	229.	289.	351.
100	63.	125.	190.	255.	355.	412.

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+17.	+27.	+41.	+88.	+75.	+63.
20	18.	29.	44.	86.	84.	89.
40	19.	31.	47.	82.	93.	118.
60	20.	33.	50.	75.	106.	148.
80	21.	35.	53.	71.	126.	183.
100	22.	37.	56.	55.	153.	220.

pressure were made before the runs at 25°, 50°, and 75°, instead of at 25° only, as usual, but this seemed to make no difference. Within the limits of error, the relation between thermal e.m.f. and pressure at any constant temperature is linear. This is surprising for so large an effect, which rises to $+ 80 \times 10^{-6}$ volts, larger than for any metal except bismuth. The maximum departure from linearity of any single point observed was 6% of the maximum effect. This point was situated at 8000 kg. and 75°; the discrepancy is almost entirely due to the width of the hysteresis loop. On changing from the curves at constant temperature to those at constant pressure, readjustments of as much as 4% were necessary. By a curious accident, the points as first plotted at each pressure lay accurately on two straight lines, intersecting at a negative temperature, the points at 0°, 25°, and 50° forming one group, and those at 75° and 100° another. I thought at first that this was due to a polymorphic transition, but a moment's consideration shows that a transition cannot produce a discontinuity in the actual ordinates of a thermal e.m.f. curve, but only an abrupt change in the direction. Such was not the case here. Zinc is also one of the substances for which Cohen [10] supposes polymorphic transitions. His transition point is at 25°, whereas here evidence of internal instability was found at every temperature above 0°.

Wagner found $+ 40 \times 10^{-12}$ volts per degree per kg. between 0° and 100° at 300 kg. This is to be compared with 70×10^{-12} deduced from the measurements above. The lack of agreement is not surprising in view of the hysteresis and its dependence on pressure. Wagner found the same hysteresis effects as were noted above, and says that the results are doubtful for this reason. With respect to this behavior he puts Zn and Cd in a class by themselves.

Magnesium. This was from the same piece of commercial magnesium as the resistance specimen, but was extruded at a different time into wire 0.020 inch diameter. The specimen whose pressure coefficient of resistance had been measured was too small and too much oxidized to use again. It was not annealed in the electric oven, as were the other newly extruded wires, for fear of too great oxidation.

The thermal e.m.f. against lead at atmospheric pressure is very small, and is given by the formulas:

$$E = (-0.095\,t + 0.00004\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (-0.095 + 0.00008\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = 0.00008(t + 273) \times 10^{-6} \text{ volts/°C}.$$

10 E. Cohen and W. D. Helderman, ZS. phys. Chem. **89**, 742–747, 1915.

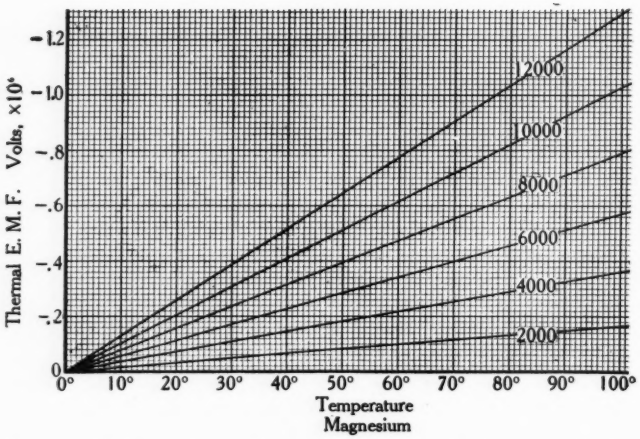

FIGURE 12. Magnesium. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.^{2} indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

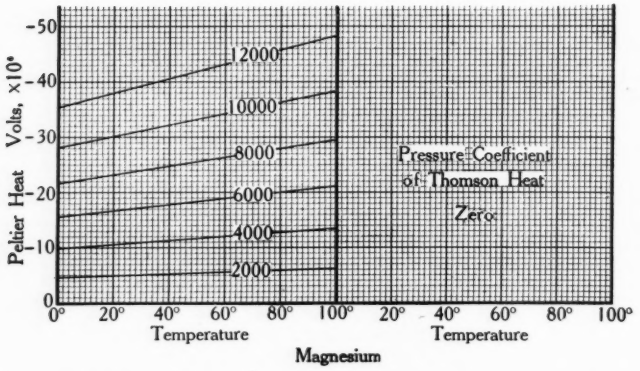

FIGURE 13. Magnesium. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. The Thomson heat of magnesium is not affected by hydrostatic pressure.

TABLE XI.

MAGNESIUM.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	−.17	−.36	−.57	−.75	−1.03	−1.30
20	.33	.72	1.04	1.58	2.06	2.59
30	.50	1.09	1.61	2.37	3.09	3.89
40	.67	1.45	2.18	3.16	4.12	5.18
50	.84	1.81	2.86	3.95	5.15	6.48
60	1.00	2.17	3.43	4.75	6.18	7.78
70	1.17	2.53	4.00	5.54	7.21	9.07
80	1.34	2.90	4.57	6.33	8.24	10.37
90	1.50	3.26	5.14	7.12	9.27	11.66
100	1.67	3.62	5.71	7.91	10.30	12.96

TABLE XII.

MAGNESIUM.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	−4.56	−9.9	−15.6	−21.6	−28.2	−35.4
20	4.91	10.6	16.7	23.3	30.2	38.0
40	5.24	11.3	17.9	24.7	32.3	40.6
60	5.56	12.1	19.0	26.3	34.3	43.2
80	5.89	12.8	20.1	27.9	36.3	45.8
100	6.23	13.5	21.1	29.6	38.4	48.4

The effect of pressure on the Thomson heat is everywhere zero.

The pressure effect on thermal e.m.f. could be measured without the sources of error which made the resistance measurements inaccurate. It is very difficult to make good electrical connections to magnesium, since it cannot be soldered, and any mechanical connection encounters the resistance of the rapidly formed layer of oxide. Any change of resistance introduces, however, no error in any potentiometer method of measuring e.m.f. like the present, so that it was possible to make e.m.f. measurements over the entire range, as for any other metal, whereas the resistance measurements could be made only at 25°. More readings were made on magnesium than on other metals because of irregularities in the earlier runs due to insufficient stirring of the ice bath. The final runs were satisfactory. The maximum zero correction was 0.75% of the maximum effect and the maximum divergence of any single observation from a smooth curve was 3.1% of the maximum, but the average numerical departure was only 0.22%. In passing from the curves at constant temperature to those at constant pressure an adjustment of the 75° curve of 3% of the maximum effect had to be made; elsewhere the readjustment was very slight.

The numerical values are shown in Tables XI and XII and Figures 12 and 13. The e.m.f. is negative and comparatively large, rising to nearly 13×10^{-6} volts at 100° and 12000 kg. The curves of e.m.f. at constant temperature against pressure are concave upwards, showing an increasing proportional effect at higher pressures, contrary to the normal behavior. At constant pressure, e.m.f. against temperature is linear. The Peltier heat is also negative, increasing numerically with both temperature and pressure. The Thomson heat is unaffected by pressure; this of course follows directly from the linearity of the effect with temperature at constant pressure.

There are no other measurements for comparison.

Aluminum. The material was freshly extruded wire of 0.02 inch diameter from the same rod as the wire on which the resistance measurements were made. The original resistance wire was too small for this purpose. The wire was annealed after extrusion by several hours at 120° in an electric oven. The effects with aluminum were so unusual that the measurements were repeated on a second specimen, this time of commercial wire. As purchased, this wire was about $\frac{1}{16}$ inch diameter; it was drawn down for this experiment through steel dies to 0.0265 inches, and annealed by heating in boiling water for about an hour.

The average temperature coefficient of resistance at atmospheric

pressure between 0° and 100° of the commercial aluminum was 0.004307. According to this test it would seem, therefore, only slightly less pure than the pure aluminum from the American Aluminum Co.; its coefficient as found in the resistance paper was 0.00434. The relation between resistance and temperature of commercial aluminum was sensibly linear.

At atmospheric pressure the thermo-electric behavior of pure aluminum against lead is given by the formulas;

$$E = (-0.416\,t + 0.00008\,t^2 - 0.00001\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (-0.416 + 0.00016\,t - 0.00003\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (0.00016 - 0.00006\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

For commercial aluminum the corresponding formulas are:

$$E = (-0.378\,t - 0.00005\,t^2 + 0.0000094\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (-0.378 - 0.0001\,t + 0.0000282\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (-0.0001 + 0.0000564\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The numerical values of the differences between the constants for these two different specimens are small, thus bearing out the observation on temperature coefficient.

Under pressure, the effects are more complicated, and for the most part very small. It would not have been possible to carry through these readings except for the perfect steadiness of the galvanometer, allowing readings to be made to the limit of sensitiveness. This was true both for the commercial and the purer samples. Wagner remarked also on the same behavior of his specimen. This is somewhat surprising, because one would be inclined at first to explain the complicated nature of the effects, which involves reversals of sign, by assuming two modifications in varying proportions. But there was no evidence whatever for any incompleteness of internal equilibrium; if there is such an effect, the change of equilibrium must occur immediately.

Measurements on the purer sample were made first. This was exposed twice to 9000 kg. at room temperature, then the apparatus taken apart to remedy a leak, and pressure then applied again twice to 12000 at 25° before beginning readings. Regular runs were made at 25°, 50°, and 75°, but at 95° the wire broke with increasing pressure, evidently because the transmitting medium was too stiff, being one half kerosene and one half ether, instead of entirely ether as usual. It was set up again with a new piece of wire, a contiguous piece from the same length as the first piece, and this was seasoned by two appli-

cations of 12000 kg. at room temperature. The point at 4000 with this agreed with the point found with the other wire before it broke. After the run at 95° with the new piece, another run with the new piece was made at 63°. This fitted smoothly between the two runs

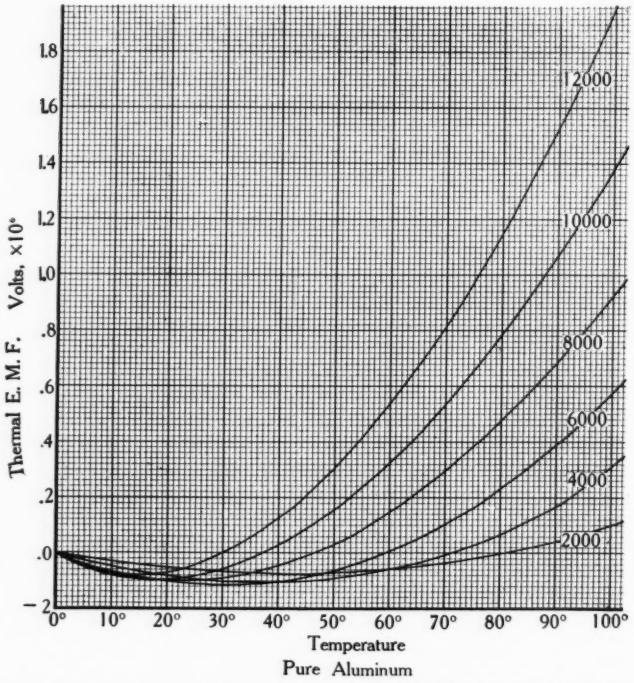

FIGURE 14. "Pure" Aluminum. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other of metal compressed to the pressure indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

with the first specimen, so that we may be confident that no error was introduced by changing pieces.

The experimental points with the purer aluminum lie smoothly. The maximum zero correction was 1.5% of the maximum effect, the maximum departure of any point from a smooth curve was 2% of

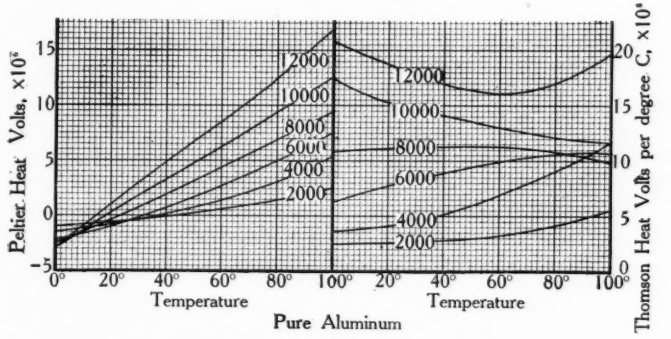

FIGURE 15. "Pure" Aluminum. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE XIII.

ALUMINUM (PURE).

Thermo-electromotive Force, volts × 10^6.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	−.031	−.048	−.068	−.070	−.076	−.069
20	−.054	−.081	−.098	−.098	−.095	−.068
30	−.068	−.100	−.114	−.089	−.056	+.003
40	−.073	−.104	−.103	−.046	+.030	+.130
50	−.070	−.091	−.063	+.032	+.158	.312
60	−.058	−.060	+.005	+.146	.328	.543
70	−.035	−.008	+.103	.296	.538	.821
80	−.002	+.066	.231	.478	.786	1.151
90	+.043	+.166	.389	.689	1.070	1.531
100	+.101	+.294	.577	.929	1.384	1.962

TABLE XIV.

Aluminum (Pure).

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	− .98	−1.48	−2.18	−2.43	−2.86	−2.86
20	− .53	− .76	− .91	− .29	+ .35	+1.03
40	− .03	+ .12	+ .78	+1.94	+3.35	+4.68
60	+ .60	+1.37	+2.73	+4.40	6.33	8.52
80	+1.41	3.10	5.07	6.94	9.39	12.42
100	2.50	5.37	7.59	9.41	12.56	16.90

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+2.4	+3.7	+6.3	+10.8	+17.5	+20.9
20	2.6	4.2	7.8	11.1	15.3	18.8
40	2.8	5.2	8.8	11.3	14.1	16.9
60	3.0	6.9	9.9	11.2	12.9	16.1
80	4.2	9.0	10.6	10.6	12.1	17.0
100	5.6	11.7	10.7	9.8	11.6	19.8

the maximum effect, and the average departure from a smooth curve was 1/2%. At the lower temperatures, 25° and 50°, where the effect is very small and the curve passes through a flat minimum, the regularity of the points is much greater. No adjustment whatever was necessary in passing from the curves at constant temperature to those at constant pressure. The numerical results are shown in Tables XIII and XIV and Figures 14 and 15. The reversals in sign and the maximum remind one of the behavior of tin, but a detailed examination shows many differences. The effect at 25° is small and negative throughout the entire range, passing through a flat minimum of about -0.1×10^{-6} volts at 6000 kg. At 50° the effect for the first 5000 kg. is much the same as at 25°, but above this it becomes rapidly different, rising through zero and reaching $+ 0.3 \times 10^{-6}$ volts at 12000 kg. At 75° the effect is positive for most of the range, and the negative minimum has been pushed back to 1500 kg. At 100° the curve probably starts out negative, but almost immediately reverses, rising to 2×10^{-6} volts at 12000 kg. At all temperatures the curves remain concave upwards. It is evident that no comparison between these results and those of Wagner is possible, because he used only one pressure, 300 kg., and one temperature interval. The effect he found was very small and negative, -0.59×10^{-12} volts per degree per kg. Since the effect is changing so rapidly it is not safe to use my results by interpolation in this region to find figures to compare with his.

The behavior of the Peltier heat is on the whole simpler than that of e.m.f. itself. The curves change sign and cross in a complicated way, but there are no maxima or minima, and the curvature is slight. The Thomson heat is still more simple; it is throughout positive. At the lower temperatures it increases regularly with pressure, but at the higher temperatures there is a rather complicated crossing of the curves.

Measurements with commercial aluminum were made only at 25°, 50°, and 75°. I would have been glad to complete the series at 95°, but after 75° the inside connection, which was merely wrapped, pulled apart, and since the purpose of the readings with this specimen was merely to see whether the effects were qualitatively the same, I did not feel justified in taking the time to set up the apparatus again. The wire was seasoned for the runs by a preliminary application of 12000 kg. at room temperature as usual. The results, as far as the broad outlines go in which aluminum is so strikingly different from other metals, were the same as for the purer specimen, but the numer-

ical details were very different. The values of e.m.f. are shown in Table XV and Figure 16; the Peltier heat and the Thomson heat are not given in detail. The effect is, as before, initially negative, the curves of e.m.f. at constant temperature passing through a very flat

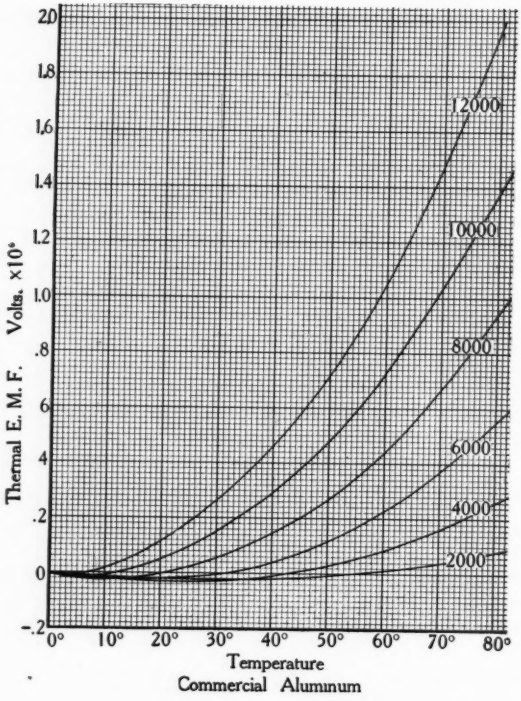

FIGURE 16. Commercial Aluminum. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

minimum and then rising. The pressure and the absolute value of the minimum both decrease rapidly at higher temperatures. The curves are throughout concave upwards. But at 25° the numerical value at the minimum is only -0.03×10^{-6} against -0.1×10^{-6} for

the purer material, and beyond the minimum the rise is much more rapid, so that at 12000 kg. the e.m.f. has become $+0.2 \times 10^{-6}$. This change of sign was not found until 50° with the purer sample. In general, the tendency towards positive values is much greater with this specimen than with the purer material. At 75°, the e.m.f. is 1.7×10^{-6} at 12000 kg., against 1.0×10^{-6} of the purer. One is tempted to generalize and say that the effect of increasing impurity

TABLE XV.

ALUMINUM (COMMERCIAL).

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	−.012	−.019	−.017	−.020	−.006	+.018
20	−.019	−.028	−.019	.000	+.050	+.116
30	−.023	−.027	−.002	+.057	+.154	.265
40	−.019	−.010	+.040	+.148	.293	.464
50	−.008	+.026	+.117	.270	.480	.720
60	+.011	+.084	.227	.440	.727	1.050
70	+.040	.162	.373	.670	1.035	1.473
80	+.080	.260	.550	.944	1.380	1.976

is to obliterate the peculiarities characteristic of aluminum itself and make the behavior approach that of a normal metal.

The Peltier heat of the impurer metal is much like that of the purer, but it passes through a greater range of values, from negative to positive, and the curvature is not so uniform. The Thomson heat is throughout positive, but much more irregular. The range of values is about the same as before, but there are maxima with respect to

temperature near 60° for all pressures above 2000 kg., and at 8000, 10000, and 12000 there are in addition minima near 30°.

Silver. The same wire was used as that on which the resistance measurements were made. The silk insulation was removed to prevent viscous drag by the transmitting fluid, and measurements were

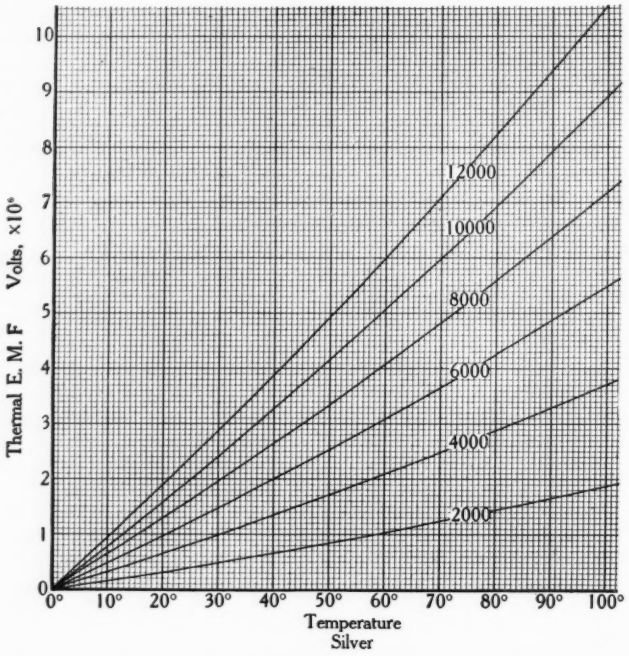

FIGURE 17. Silver. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

made on five strands in parallel. The use of strands in parallel has several advantages; it reduces viscous drag, reduces danger of breakage during handling (the wire was 0.003 inch in diameter), and reduces the resistance of the circuit so that the galvanometer is more sensitive.

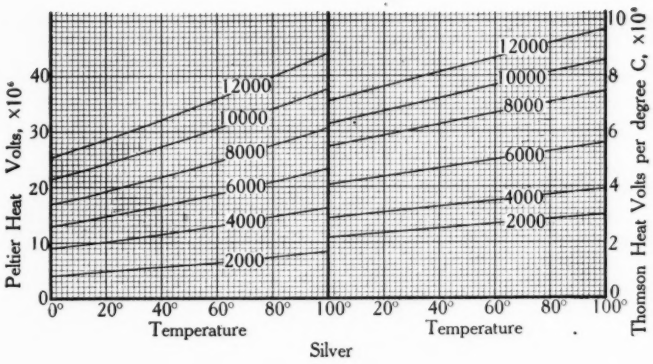

FIGURE 18. Silver. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE XVI.

SILVER.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+.15	+.32	+.48	+.63	+.79	+.94
20	.31	.66	.97	1.28	1.60	1.90
30	.48	1.00	1.48	1.95	2.43	2.89
40	.66	1.36	2.00	2.64	3.29	3.91
50	.84	1.72	2.54	3.35	4.17	4.95
60	1.03	2.10	3.10	4.08	5.07	6.02
70	1.23	2.49	3.67	4.83	5.99	7.12
80	1.44	2.89	4.26	5.60	6.94	8.24
90	1.65	3.30	4.87	6.38	7.91	9.39
100	1.87	3.72	5.49	7.19	8.91	10.56

TABLE XVII.

SILVER.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+3.9	+8.9	+12.9	+16.9	+21.6	+25.3
20	4.8	10.1	14.6	19.3	24.1	28.5
40	5.6	11.4	16.6	21.9	27.4	32.1
60	6.5	12.8	18.8	24.6	30.5	36.0
80	7.4	14.5	21.0	27.5	33.9	40.0
100	8.4	16.1	23.3	30.6	37.6	44.2

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+2.2	+2.9	+4.1	+5.5	+6.3	+7.1
20	2.3	3.1	4.4	5.9	6.7	7.6
40	2.5	3.3	4.7	6.3	7.2	8.1
60	2.7	3.5	5.0	6.7	7.7	8.7
80	2.8	3.7	5.3	7.1	8.1	9.2
100	3.0	3.9	5.6	7.5	8.6	9.7

The thermo-electric behavior at atmospheric pressure against lead is given by the formulas:

$$E = (2.556\,t + 0.00432\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (2.556 + 0.00864\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = 0.00864(t + 273) \times 10^{-6} \text{ volts/°C}.$$

For the pressure measurements it was seasoned in the regular way by two applications of 12000 kg. at room temperature. The readings under pressure went perfectly smoothly, without incident of any sort. The maximum zero correction was at 98°, 0.7% of the maximum effect; there was only one bad point, at 10000 kg. and 75°, where there was a discrepancy of 2.5%. Except for this, the maximum departure of any point was 1.2%, and the average arithmetical departure from a smooth curve was only 0.11%. In changing from the curves at constant temperature to those at constant pressure the maximum readjustment necessary was 0.3%.

The numerical results are shown in Tables XVI and XVII and Figures 17 and 18. At constant temperature the curves of e.m.f. against pressure are concave toward the pressure axis, which is what one would expect. At constant pressure, on the other hand, the curves are convex toward the pressure axis. The e.m.f. is positive and increases regularly with pressure and temperature. The Peltier heat is positive and increases regularly with pressure and temperature. The Thomson heat is also positive; it increases with rising pressure, and at any constant pressure is proportional to the absolute temperature.

Wagner gives up to 300 kg. and between 0° and 100° $+ 8.7 \times 10^{-12}$ volts per degree per kg., against 9.3×10^{-12} interpolated from the data above.

Gold. This was the same piece of wire whose resistance was measured under pressure. It was used bare, in parallel strands. The runs at 25°, 50°, and 75° were with four strands, but at 97° two only were used because the other two had been accidentally broken during manipulation.

The thermo-electric behavior at atmospheric pressure against lead is given by the formulas:

$$E = (2.899\,t + 0.00467\,t^2 - 0.00000166\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (2.899 + 0.00934\,t - 0.00000498\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (0.00934\,t - 0.00000996\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The manipulation demanded by the pressure measurements was difficult because of the great fragility of the wire, which was only

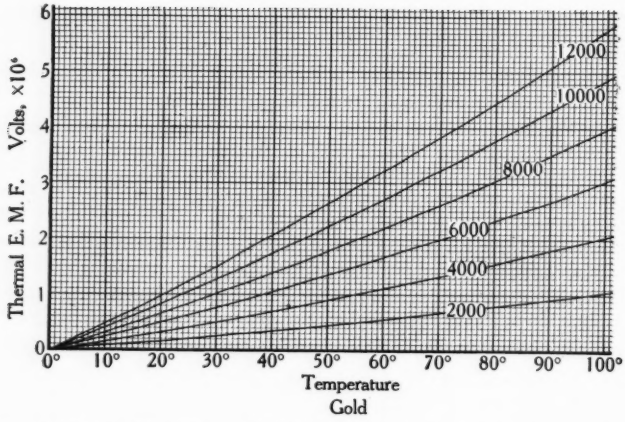

FIGURE 19. Gold. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other at the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

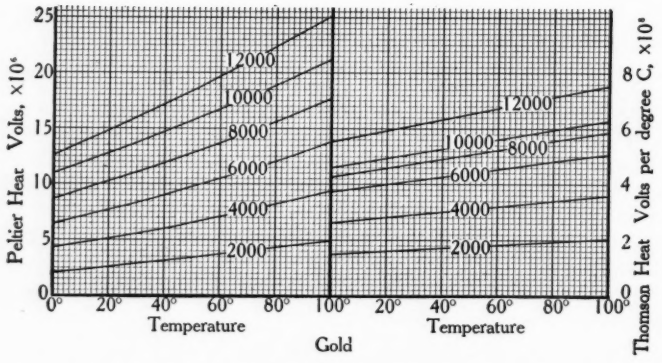

FIGURE 20. Gold. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

0.004 inch in diameter. Before the runs the wire was seasoned by a single application of 12000 kg. at room temperature. At the first run at 25° all four strands broke at the lower end above 8000 kg., possibly due to cutting by the glass insulating covering during the small motion necessarily incident to change of pressure. The apparatus was set up again, and three runs successfully made at 25°, 50°, and 75°, but after 75° two of the strands broke, because of imperfect functioning of the bye-pass on release of pressure, and the run at 97° was made with the remaining two strands.

The measurements of e.m.f. were regular and satisfactory. Equili-

TABLE XVIII.

GOLD.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+.080	+.162	+.242	+.327	+.411	+.485
20	.165	.333	.498	.670	.839	.990
30	.257	.514	.767	1.028	1.284	1.515
40	.354	.705	1.049	1.402	1.745	2.061
50	.456	.905	1.345	1.791	2.224	2.627
60	.564	1.115	1.655	2.196	2.719	3.213
70	.678	1.334	1.978	2.617	3.230	3.819
80	.797	1.563	2.315	3.054	3.760	4.446
90	.922	1.802	2.665	3.506	4.305	5.093
100	1.052	2.051	3.029	3.974	4.867	5.760

brium was rapidly reached, and there was no unsteadiness or other evidence of internal instability. The maximum departure of any observed point from a smooth curve was 1.3% of the maximum effect, and the average arithmetical departure was 0.2%. The maximum readjustment necessary in passing from curves at constant temperature to those at constant pressure was 0.86%.

The numerical values are shown in Tables XVIII and XIX and Figures 19 and 20. The e.m.f. is positive, increasing regularly with pressure and temperature to 5.76×10^{-6} volts at 100° and 12000 kg.

TABLE XIX.

GOLD.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+2.1	+4.3	+6.4	+8.7	11.0	13.0
20	2.6	5.2	7.7	10.3	12.8	15.1
40	3.1	6.1	9.1	11.9	14.8	17.4
60	3.7	7.1	10.5	13.7	16.8	19.8
80	4.3	8.2	12.1	15.7	18.9	22.5
100	4.9	9.4	13.8	17.8	21.3	25.2

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C, $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+1.5	+2.6	+3.7	+4.3	+4.6	+5.5
20	1.6	2.8	4.0	4.6	4.9	5.9
40	1.7	3.0	4.25	4.9	5.25	6.3
60	1.8	3.2	4.5	5.2	5.6	6.7
80	1.9	3.4	4.8	5.5	5.9	7.1
100	2.0	3.6	5.1	5.9	6.3	7.5

The pressure effects on Peltier heat and Thomson heat are both positive, and both increase regularly with pressure and temperature. At constant pressure the Thomson heat is proportional to absolute temperature.

Wagner found between 0° and 100° and up to 300 kg. $+ 4.6 \times 10^{-12}$ volts per degree per kg. The value indicated by interpolation of the data above is 5.3×10^{-12}.

Copper. This was electrolytic copper from the same length of wire as that whose resistance was measured under pressure, but not

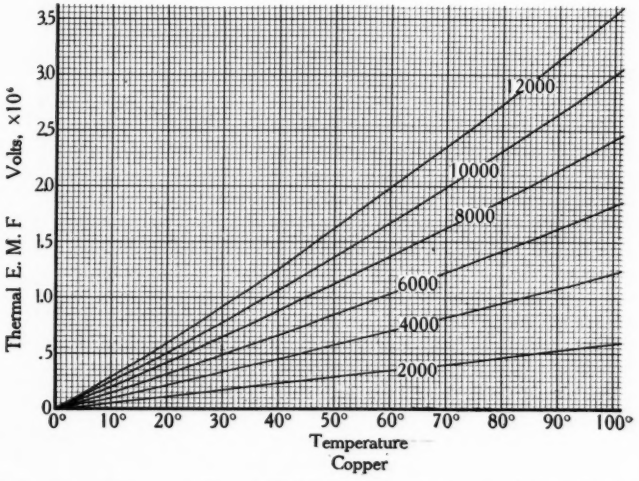

FIGURE 21. Copper. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being 0°C and the temperature plotted as abscissae.

the identical piece of wire. It was drawn down to 0.028 inch in diameter through steel dies, annealed to redness, and the surface rubbed off with emery paper.

At atmospheric pressure its thermo-electric behavior against lead is given by the formulas:

$$E = (2.777\,t. + 0.00483\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (2.777 + 0.00966\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = 0.00966(t + 273) \times 10^{-6} \text{ volts/°C}.$$

This electrolytic copper did not differ greatly in thermo-electric properties from commercial copper. The thermal e.m.f. of electrolytic against commercial copper was found to be given by the expression:

$$E = (0.03468\,t + 0.0000133\,t^2) \times 10^{-6} \text{ volts.}$$

The measurements under pressure went satisfactorily, but the results were somewhat more irregular than usual because of the smallness

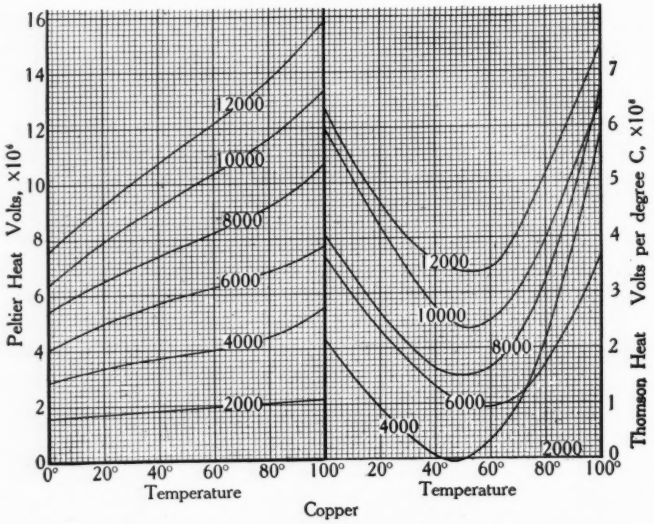

FIGURE 22. Copper. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

of the effect. The maximum zero correction was 1.5% of the maximum effect; this was also the maximum departure of any point from a smooth curve. The average arithmetical departure of all the observed points from a smooth curve was 0.31%. The maximum readjustment necessary in passing from the constant temperature to the constant pressure curves was 0.8%.

The numerical results are shown in Tables XX and XXI and Figures 21 and 22. At constant temperature the e.m.f. curves are nearly linear, but are slightly concave toward the pressure axis, as is natural. At constant pressure the e.m.f. curves are convex toward the temperature axis. The thermal e.m.f. is positive, rises regularly with pressure and temperature to 3.546×10^{-6} volts at 100° and 12000 kg. The Peltier heat is positive and rises with pressure and temperature. The Thomson heat is zero at the lower pressures, becomes

TABLE XX.

COPPER.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+.058	+.110	+.154	+.206	+.244	+.288
20	.117	.224	.318	.424	.506	.596
30	.175	.340	.490	.650	.784	.918
40	.234	.460	.668	.884	1.072	1.256
50	.292	.580	.852	1.124	1.372	1.616
60	.350	.700	1.038	1.370	1.678	1.976
70	.409	.822	1.226	1.620	1.994	2.348
80	.467	.946	1.418	1.876	2.318	2.732
90	.526	1.076	1.624	2.142	2.654	3.130
100	.584	1.216	1.828	2.420	3.004	3.546

positive at the higher, and at each constant pressure passes through a minimum with rising temperature.

The value found by Wagner between 0° and 100° at 300 kg. was $+ 3.2 \times 10^{-12}$ volts per degree per kg. against 2.9×10^{-12} indicated by interpolation of the data above.

Copper is one of the metals for which Cohen[11] finds allotropic forms. No evidence of this has been found by Burgess and Kellberg,[12] however, from measurements of electrical resistance, and my thermal e.m.f. measurements above also suggest nothing of the kind.

11 E. Cohen and W. D. Helderman, ZS. phys. Chem. **89**, 638–639, 1915.
12 G. K. Burgess and I. N. Kellberg, Jour. Wash. Acad. Sci. **5**, 657–662, 1915.

TABLE XXI.

COPPER.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+1.6	+2.9	+4.1	+5.4	+6.4	+7.6
20	1.7	3.4	5.0	6.5	7.9	9.3
40	1.8	3.7	5.7	7.4	9.2	10.8
60	1.9	4.0	6.3	8.2	10.4	12.2
80	2.1	4.4	6.8	9.2	11.6	13.7
100	2.2	5.5	7.8	10.7	13.4	15.9

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Tem C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	0	+2.2	+3.7	+4.1	+6.0	+6.3
20	0	.9	2.3	2.6	4.2	4.7
40	0	+ .1	1.3	1.6	2.7	3.5
60	0	+ .4	1.0	1.7	2.5	3.4
80	0	2.3	1.8	3.3	4.2	5.2
100	0	6.0	3.8	6.7	6.5	7.5

Nickel. This was the same piece of wire as that whose resistance under pressure was measured. The insulation was stripped, and it was used in five parallel strands of bare wire. The points obtained are not as regular as could be desired because of failure of the tempera-

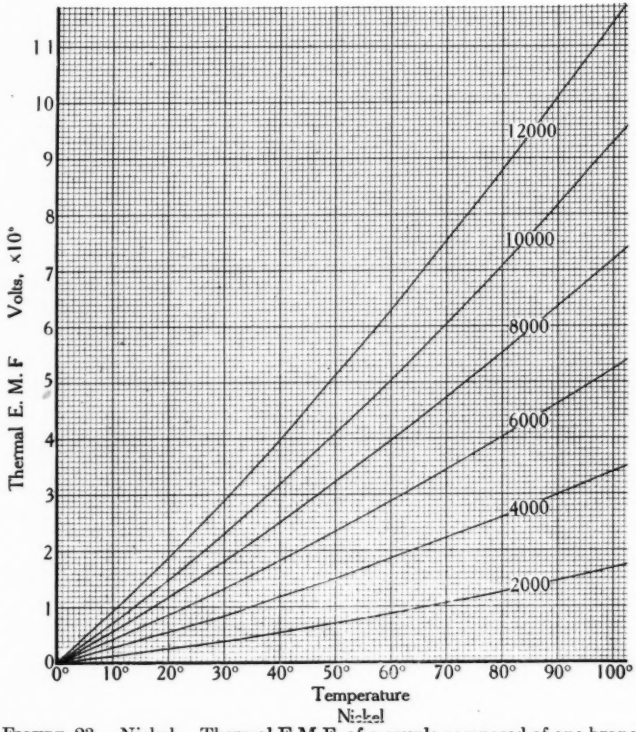

FIGURE 23. Nickel. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, one junction being at 0°C and the other at the temperature plotted as abscissae.

ture regulator to work perfectly. The regulator was cleaned after these runs, and was again perfectly satisfactory. It did not seem worth while to repeat the runs on nickel for the sake of the slightly greater obtainable accuracy.

At atmospheric pressure the thermal behavior against lead is given by formulas:

$$E = (-17.61\,t - 0.0178\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (-17.61 - 0.0356\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = -0.0356(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The measurements under pressure went without incident except for somewhat greater irregularities than usual due to imperfection

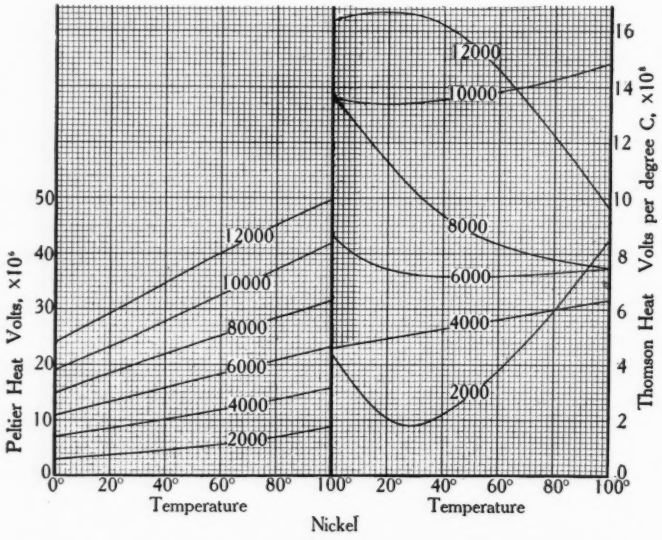

FIGURE 24. Nickel. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicate on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

of temperature control already mentioned. The pressure manipulation of this substance was a matter of some difficulty, because temporary effects due to elastic drag are easy to get. There was no evidence of incomplete internal equilibrium. The maximum zero correction was 1% of the total effect, and the maximum departure of any single

observed point from a smooth curve was 3.6%, and the average arithmetical departure 0.72%. The maximum adjustment in passing from constant temperature to constant pressure curves was 2.3%.

The numerical results are shown in Figures 23 and 24 and Tables XXII and XXIII. At constant temperature the e.m.f. curves are convex toward the pressure axis, which is unusual, but at constant pressure the curvature is convex toward the temperature axis, as is normal. The e.m.f. is positive, increasing regularly with pressure and temperature to 11.4×10^{-6} volts at 100° and 12000 kg., but it is

TABLE XXII.

NICKEL.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+.12	+.27	+.41	+.56	+.73	+.91
20	.25	.55	.85	1.17	1.50	1.88
30	.39	.85	1.32	1.82	2.32	2.91
40	.54	1.17	1.82	2.51	3.19	4.00
50	.70	1.50	2.34	3.23	4.10	5.14
60	.87	1.85	2.88	3.97	5.05	6.32
70	1.05	2.21	3.44	4.74	6.05	7.55
80	1.25	2.59	4.02	5.53	7.09	8.81
90	1.45	2.99	4.62	6.35	8.17	10.11
100	1.68	3.40	5.24	7.19	9.29	11.44

not as large as one would expect from the thermo-electric activity of nickel against other metals at atmospheric pressure. The Peltier heat is positive, increasing with pressure and temperature. The Thomson heat is also positive, but at low pressures it passes through a minimum with rising temperature and at high pressures it decreases over the entire range with increasing temperature.

Wagner's value up to 300 kg. between 0° and 100° is $+ 9.6 \times 10^{-12}$ volts per degree per kg. against 8.4 interpolated from the data above. The difference may well be due at least in part to insufficient purity of my specimen.

TABLE XXIII.

NICKEL.

Peltier heat, from uncompressed to compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+3.0	+7.1	+10.9	+14.8	+19.1	+24.1
20	3.9	8.5	13.2	18.4	23.2	29.3
40	4.7	10.2	15.8	21.9	27.7	34.7
60	5.7	11.8	18.3	25.3	32.5	40.1
80	7.1	13.8	20.8	28.4	37.2	45.1
100	8.9	15.7	23.3	31.5	42.1	49.9

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+4.4	+4.6	+8.6	+13.7	+13.6	+16.4
20	2.1	5.0	7.4	11.3	13.4	16.5
40	2.2	5.3	7.2	9.4	13.5	16.2
60	3.8	5.6	7.2	8.3	13.8	14.6
80	6.0	6.0	7.3	7.8	14.3	12.2
100	8.6	6.3	7.5	7.5	14.9	9.6

Cobalt. This was from the same length as the resistance specimen, but was not the identical piece. Part of this wire had not been previously annealed, and it was therefore annealed before these runs exactly as was the resistance piece. Five strands in parallel were

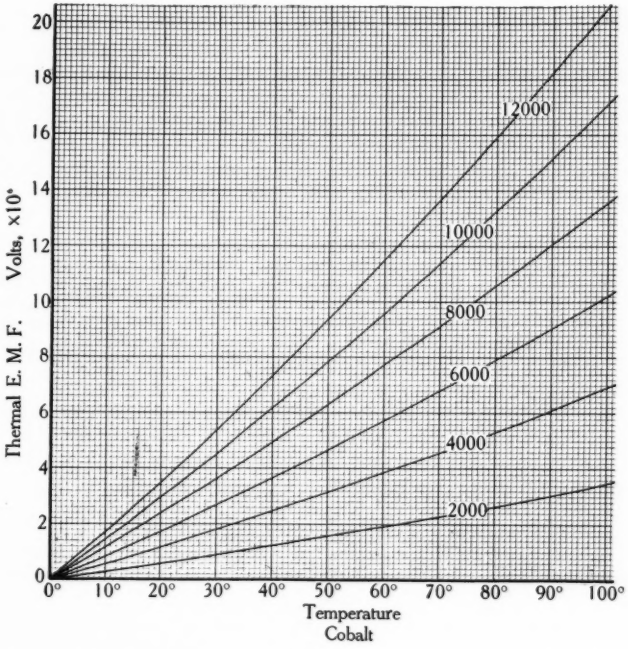

FIGURE 25. Cobalt. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

used, insulated as usual with short pieces of glass. The wire is more inhomogeneous than most of the other metals, as was shown by the rather large permanent zero effect, which was two or three times larger than the total pressure effect. However, the permanent zero remained so constant that fairly good measurements could be obtained.

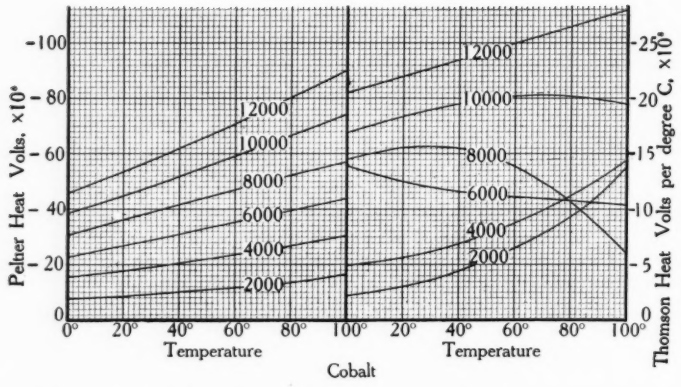

FIGURE 26. Cobalt. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicate on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE XXIV.

COBALT.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	−.29	−.59	−.86	−1.16	−1.44	−1.72
20	.59	1.20	1.76	2.37	2.95	3.52
30	.90	1.83	2.71	3.63	4.52	5.39
40	1.22	2.48	3.69	4.94	6.15	7.34
50	1.56	3.16	4.71	6.30	7.84	9.37
60	1.91	3.86	5.75	7.70	9.59	11.47
70	2.27	4.58	6.82	9.13	11.40	13.65
80	2.65	5.33	7.92	10.59	13.26	15.90
90	3.05	6.11	9.05	12.08	15.18	18.22
100	3.48	6.92	10.21	13.60	17.15	20.61

TABLE XXV.

Cobalt.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	−7.6	−15.8	−22.7	−30.8	−38.5	−45.9
20	8.8	18.2	26.9	36.1	44.9	53.6
40	10.3	20.7	31.3	41.6	52.0	62.2
60	11.6	23.7	35.3	47.3	59.4	71.0
80	13.8	26.8	39.5	52.3	66.7	80.3
100	16.8	30.9	44.0	57.0	74.6	90.5

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	−2.2	−4.9	−13.9	−14.5	−16.9	−20.5
20	2.9	5.6	12.6	15.5	18.5	22.0
40	4.4	6.9	11.6	15.3	19.4	23.5
60	6.7	8.7	11.3	13.7	20.0	25.0
80	9.2	11.3	10.9	10.6	20.1	26.4
100	13.8	14.5	10.4	6.0	19.4	28.0

At atmospheric pressure the thermal electric behavior against lead is given by the formulas:

$$E = (-17.32\,t - 0.0390\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (-17.32 - 0.078\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = -0.078(t + 273) \times 10^{-6} \text{ volts/°C}.$$

For the pressure measurements it was seasoned twice at room temperature to 12000 kg. Successful runs were made at 25°, 50°, 75°, and 97°. At 97° the zero was displaced by an unusually large amount after the run. This displacement apparently had no connection with the other readings, and was probably accidental; this point was discarded. Except for this point, the maximum zero correction was 1.5% of the total effect, the maximum departure of any point from a smooth curve was 4.5%, and the average arithmetical departure 0.81%. The maximum readjustment in going from curves at constant temperature to those at constant pressure was 1%.

The numerical results are shown in Tables XXIV and XXV and Figures 25 and 26. The effect is negative and large, increasing regularly with pressure and temperature to -20.61×10^{-6} at 12000 kg. and 100°. The Peltier heat is negative, increasing in magnitude with pressure and temperature. The Thomson heat is also negative, in general increasing in magnitude with pressure and temperature, but at the highest temperature it passes through a pressure minimum near 8000 kg.

There are no previous results for comparison. Cobalt has the largest negative effect of any metal measured. One would expect anomalies because of the unusually large Thomson heat at atmospheric pressure.

Iron. Three different samples of iron were used; the effects were complicated as for tin and aluminum, and it therefore seemed desirable to find how the effect varied with different material. The first sample was of American Ingot Iron, from the same piece as that of the resistance measurements under pressure. It was drawn down to 0.020 inch diameter, and annealed to redness in the air. Except for the difference of diameter, this was the same treatment as the resistance specimen received. Another specimen of the same wire was used, but it was left unannealed after drawing from 0.017 to 0.0105 inches in diameter. Its average temperature coefficient between 0° and 100° at atmospheric pressure was 0.006080, against 0.006206 for the same material when annealed. The third specimen was a commercial soft iron wire such as is used for binding hay bales etc. It

was drawn from 0.06 to 0.03 inches diameter, and annealed to redness after the final drawing. The commercial wire must have been of unusual purity, because the average temperature coefficient of resistance at atmospheric pressure between 0° and 100° had the high value 0.00596, and its resistance shows the same striking departure from linearity with temperature as does the pure iron.

At atmospheric pressure the thermal electric behavior of these various specimens against lead is given by the following formulas. Ingot iron, annealed,

$$E = (16.18\,t - 0.0089\,t^2 - 0.000086\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (16.18 - 0.0178\,t - 0.000258\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (-0.0178 - 0.000516\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

Ingot iron, hard drawn,

$$E = (15.92\,t - 0.0106\,t^2 - 0.000056\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (15.92 - 0.0212\,t - 0.000168\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (-0.0212 - 0.000336\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

Commercial iron, annealed,

$$E = (16.56\,t - 0.0033\,t^2 - 0.000122\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (16.56 - 0.0066\,t - 0.000366\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (-0.0066 - 0.000732\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The behavior of these different specimens is therefore not unlike.

Under pressure, each specimen was subjected to the same treatment. They were seasoned twice by applications of 12000 kg. at room temperature, and runs were then made as usual at 25°, 50°, 75°, and 95°. The behavior of all was qualitatively the same, with numerical differences. A longer time than normal was always required to reach steady readings, and there were rather large irregularities, suggesting that all three samples were in a state of incomplete internal equilibrium. This is what would be expected from the behavior of iron in other particulars.

Of course the greatest interest attaches to the annealed ingot iron, this approaching most closely to pure iron in a state of complete ease. Even this shows much hysteresis, which increases greatly at the higher temperatures. At 25°, the e.m.f. is negative throughout, and is small. For the first 4000 kg. the curve is exceedingly flat, and hugs the axis closely. The curvature is downward, the negative effect increasing numerically by larger fractions of itself for equal pressure increments at the higher pressures. At 25° the hysteresis is one eighth of the

total effect at 25°. At 50° the e.m.f. is throughout positive, but the direction of curvature is the same as at 25°, which allows a maximum at about 6000 kg. The effect at 50° does not at its maximum attain one half the numerical value at 25°, and the hysteresis at 50° is one third the total effect at 50°. At 75° the effect is much larger; the curvature is the same, and the maximum has disappeared. The indications are that there is a maximum at some much higher pressure

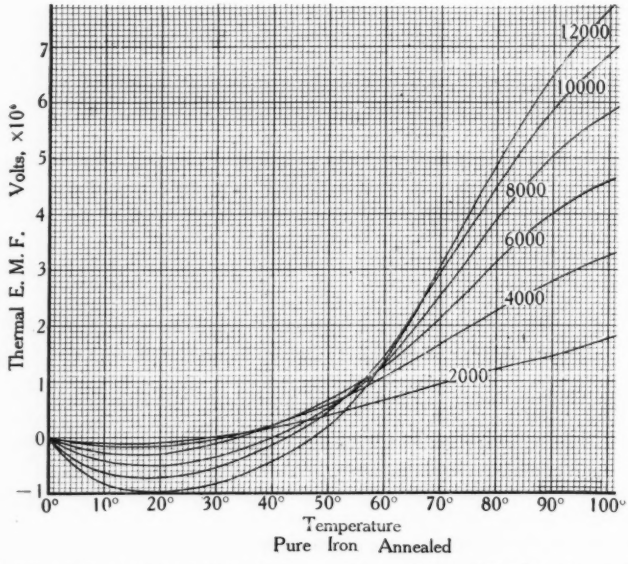

FIGURE 27. American Ingot Iron, Annealed. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

than 12000 kg. The hysteresis at 75° is 12% of the maximum at 75°. At 75° and 50° the hysteresis is abnormal in direction, being a hastening forward instead of a lagging behind. It should properly not be called a hysteresis at all; and must be due to a different kind of failure of internal equilibrium from the ordinary effect. At 99° the character of the curve is the same as at 75°; the greatest e.m.f. is twice that at

75°, and the hysteresis is about the same fraction of itself, but is in the normal direction. No readjustment was necessary in passing from the constant temperature to the constant pressure curves.

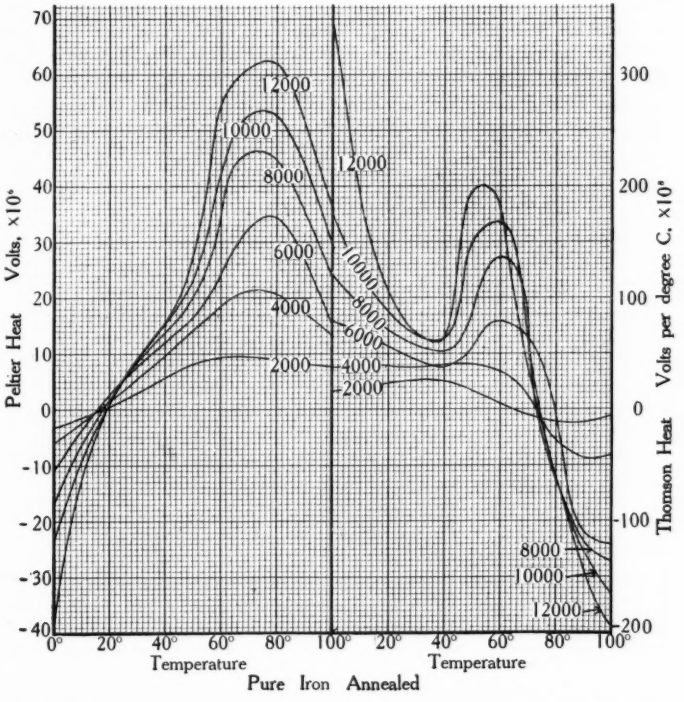

FIGURE 28. American Ingot Iron, Annealed. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

The numerical results are shown in Tables XXVI and XXVII and Figures 27 and 28. The Peltier heat is at first negative at all pressures, becomes positive with increasing temperature, passes through a posi-

tive maximum and decreases. The behavior of the Thomson heat is complicated. On the whole the course is, at every pressure, from positive values at 0° to negative values at 100°, but near 40° the normal course is arrested, the effect reversing in direction and passing through a maximum between 50° and 60°, and then resuming its fall to negative values.

It will not pay to go into the behavior of the other two specimens in such detail. Tables and diagrams are given showing the e.m.f. but not the Peltier and the Thomson heats. Both showed qualitatively the same behavior as the pure specimen; the effect was negative at

TABLE XXVI.

IRON (PURE, ANNEALED).

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	−.08	−.15	−.27	−.42	− .64	− .84
20	−.08	−.15	−.28	−.50	− .74	− .99
30	+.03	−.02	−.10	−.34	− .54	− .81
40	+.17	+.22	+.22	+.02	− .13	− .41
50	.39	+.59	+.67	+.53	+ .46	+ .22
60	.66	1.08	1.27	1.31	+1.45	+1.40
70	.94	1.67	2.14	2.57	2.94	3.08
80	1.21	2.28	3.15	3.91	4.48	4.89
90	1.45	2.81	4.03	5.03	5.85	6.49
100	1.67	3.25	4.60	5.82	6.86	7.68

low temperatures (plotted against pressure), rising to normally high positive values at 100°. The direction of curvature is the same as for the annealed iron, but the anomaly in direction of hysteresis was not repeated. The hysteresis effects were of about the same magnitude as for the first specimen, except that at 95° the hard drawn specimen showed large permanent changes. This is not surprising. The numerical values of thermal e.m.f. against temperature at constant pressure are plotted in Figures 29 and 30. At low temperature all three sets of curves for the three specimens are alike, but between 75° and 100° the hard drawn and the commercial iron do not show the

TABLE XXVII.

IRON (PURE, ANNEALED).

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	−3.3	−6.0	−10.9	−16.9	−23.3	−38.3
20	+ .9	+1.8	+ 2.6	+ 1.8	+ 1.2	+ 1.2
40	+5.6	+9.7	+12.2	+13.8	+15.4	+15.7
60	+9.3	18.3	24.7	34.0	42.6	50.0
80	8.8	20.4	34.3	44.5	52.4	62.2
100	7.5	13.1	14.9	23.1	29.4	35.8

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.² 4000	4000	6000	8000	10000	12000
0°	+17.	+38.	+ 79.	+120.	+175.	+347.
20	23.	38.	56.	72.	88.	106.
40	25.	41.	37.	52.	63.	63.
60	5.	33.	79.	137.	167.	180.
80	−10.6	−28.	− 11.	− 63.	− 64.	− 56.
100	− 5.6	−41.	−121.	−136.	−166.	−194.

reversal in direction of curvature that the annealed iron does. The numerical values are also very different. At 100° and 12000 kg. the thermal e.m.f. of soft ingot iron is 7.68×10^{-6}, of hard drawn ingot iron 12.80, and of annealed commercial iron 9.56. The mechanical treatment apparently makes more difference than slight differences in chemical composition.

It is not worth while to give the Peltier and Thomson heats of these two other specimens; if any one is especially interested they may be

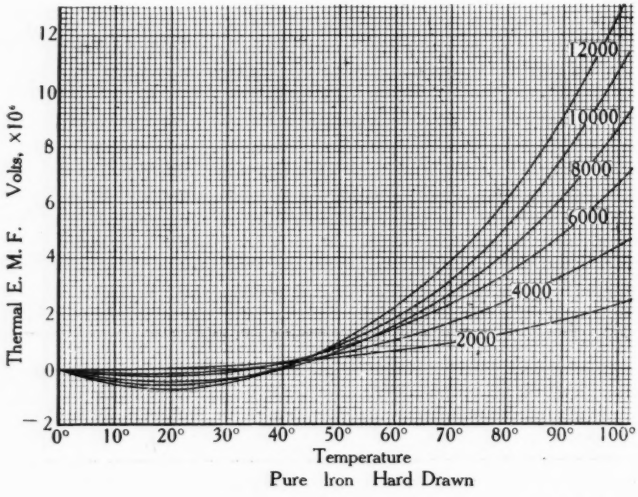

FIGURE 29. American Ingot Iron, Hard Drawn. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

obtained by calculation from the curves, or I will be glad personally to send him the figures. The general character of the effects is quite different from that of the annealed pure iron, due to the reversal in curvature of pure iron between 75° and 100° already mentioned. The Peltier heat of both of these specimens rises from initial negative values to high positive values. The general course of the Thomson heat is from low to high positive values with rising pressure and temperature, but both specimens show minima near 40°.

Previous measurements by Wagner were only to 300 kg. and from 0° to 100°. Of course he could not suspect the complicated actual state of affairs, and comparison of our results is of little use. He

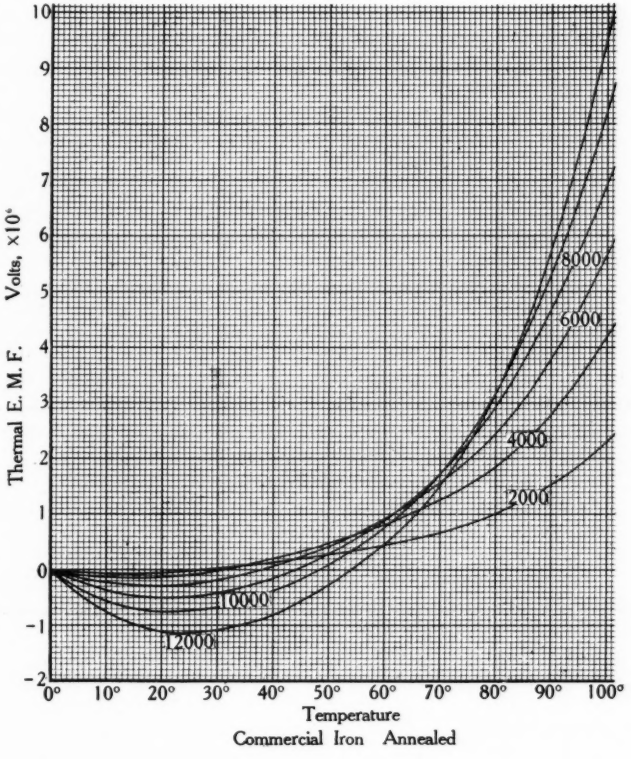

FIGURE 30. Commercial Iron, Annealed. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

found $+ 12.5 \times 10^{-12}$ volts per degree per kg. against $+ 8.3 \times 10^{-12}$ interpolated from the data above for annealed pure iron. His value would correspond more with my value for the hard drawn specimen.

TABLE XXVIII.

IRON (PURE, HARD-DRAWN).

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	−.01	−.13	−.21	−.35	−.43	−.57
20	+.02	−.15	−.24	−.45	−.54	−.74
30	+.10	−.05	−.11	−.36	−.37	−.54
40	.23	+.18	+.21	−.02	+.10	+.01
50	.40	+.55	+.74	+.63	+.86	+.95
60	.62	1.04	1.43	+1.54	1.85	2.20
70	.91	1.66	2.30	2.69	3.20	3.85
80	1.27	2.42	3.40	4.20	5.11	6.12
90	1.73	3.34	4.83	6.17	7.59	9.05
100	2.30	4.42	6.69	8.70	10.70	12.80

TABLE XXIX.

IRON (COMMERCIAL).

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	−.04	−.11	−.22	−.37	−.55	−.75
20	−.03	−.11	−.29	−.50	−.75	−1.12
30	+.04	.00	−.19	−.42	−.69	−1.10
40	+.15	+.22	+.07	−.15	−.40	−.82
50	.29	+.50	+.44	+.30	+.07	−.28
60	.46	.82	.93	+.88	+.75	+.44
70	.68	1.25	1.57	1.72	1.72	+1.52
80	1.02	1.85	2.47	2.94	3.18	3.19
90	1.55	2.79	3.82	4.69	5.33	5.79
100	2.34	4.20	5.68	6.94	8.25	9.56

Palladium. This was the same piece of wire whose pressure coefficient of resistance was measured. The silk insulation was removed, and it was used in three parallel strands; there was not enough material at hand to use more than three strands. More trouble from breakage was found with this substance than with any other. Twice during the runs it broke, and the apparatus had to be taken apart and set up again. Fortunately the breaks occurred at the end of the wire, so that it was sufficient merely to resolder them. The breakage was probably intimately connected with the small size of the wire and the small number of strands. Much care had to be

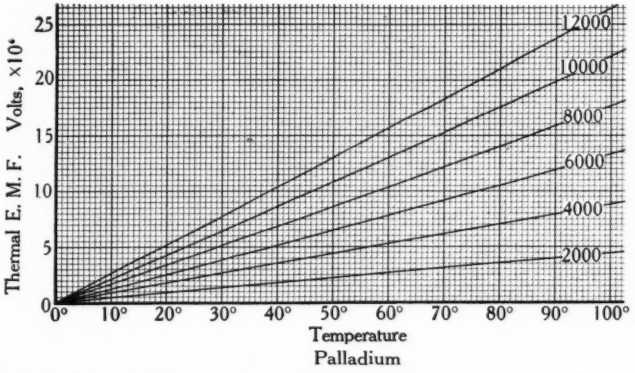

FIGURE 31. Palladium. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

taken to so manipulate the pressure as to avoid tension effects from viscous drag.

At atmospheric pressure its thermo-electric behavior against lead is given by the formulas:

$$E = (-5.496\,t - 0.01760\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (-5.496 - 0.0352\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = -0.0352(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The readings under pressure went smoothly, except for the two breaks mentioned. The irregularities were somewhat greater than normal; probably the effect of viscous drag was not entirely elimi-

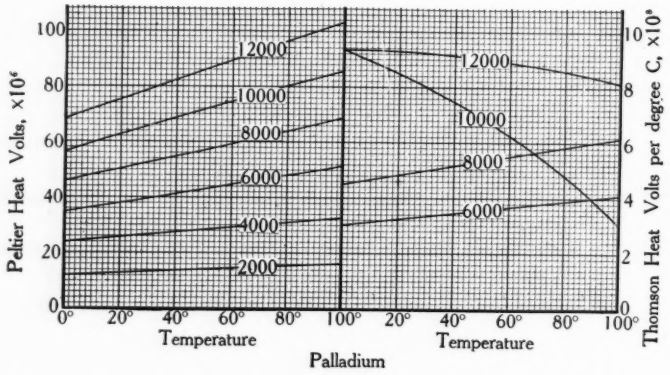

FIGURE 32. Palladium. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE XXX.

PALLADIUM.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+.44	+.88	+1.28	+1.69	+2.10	+2.53
20	.88	1.76	2.57	3.40	4.23	5.09
30	1.32	2.64	3.87	5.13	6.39	7.69
40	1.75	3.52	5.18	6.87	8.58	10.32
50	2.19	4.40	6.51	8.63	10.80	12.97
60	2.63	5.28	7.85	10.41	13.04	15.64
70	3.07	6.16	9.20	12.21	15.30	18.33
80	3.50	7.04	10.56	14.02	17.57	21.04
90	3.94	7.92	11.93	15.85	19.85	23.77
100	4.38	8.80	13.31	17.69	22.14	26.52

TABLE XXXI.

Palladium.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+12.0	+24.0	+34.9	+46.0	+56.7	+68.5
20	12.9	25.8	38.1	50.5	62.7	75.3
40	13.8	27.5	41.4	54.8	68.8	82.4
60	14.6	29.3	44.6	59.4	74.6	89.0
80	15.5	31.0	48.2	64.2	80.3	96.0
100	16.4	32.8	51.7	69.0	85.6	103.4

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	0	0	+3.0	+4.5	+9.3	+9.3
20	0	0	3.2	4.8	8.5	9.4
40	0	0	3.4	5.2	7.5	9.1
60	0	0	3.7	5.5	6.3	9.0
80	0	0	3.9	5.8	4.9	8.5
100	0	0	4.1	6.2	3.0	8.2

nated. The zero corrections were negligible; the maximum deviation of any single reading from a smooth curve was 3% of the total effect, and the average numerical departure was 0.47%. The maximum readjustment in passing from constant temperature to constant pressure curves was 0.27%.

The numerical results are shown in Tables XXX and XXXI and Figures 31 and 32. Both at constant pressure and constant temperature the e.m.f. curves are nearly linear. The e.m.f. is positive and one of the largest found, rising to 26.5×10^{-6} volts at 100° and 12000 kg. The Peltier heat is positive, rising regularly with pressure and temperature. The Thomson heat above 5000 kg. is positive, falling with rising temperature at the higher pressures and rising at the lower pressures. Below 5000 kg. it is approximately zero.

The value given by Wagner at 300 kg. between 0° and 100° was $+23.7 \times 10^{-12}$ volts per degree per kg. against 21.9×10^{-12} interpolated from the data above.

Platinum. Readings were made on the same piece of Heraeus platinum, loaned by Professor H. N. Davis, as were the resistance measurements under pressure. I wanted to procure especially good data for platinum, because so much work has been done on its other physical properties, but unfortunately the results are among the most unsatisfactory. The piece was so short that only one strand could be used, and even then an especial procedure had to be adopted to make the outside connections. Furthermore, the wire had been previously used for a resistance thermometer, wound on a small mica frame, and it was consequently full of small tortuosities which could not be removed without danger of altering the properties of the wire. The roughness of the wire and its small size conspired to make the tension effects of viscous drag particularly high. The same effect was responsible for the wire breaking during the application of seasoning pressure at room temperature. It was fused together again by arcing. The viscous drag might give rise to an error of as much as 20% in the total effect, but this can be very greatly cut down by careful manipulation.

In addition to the measurements on Heraeus platinum, a complete series of readings was also made on an impurer sample from Baker. The pressure effect on the resistance of this has also been measured previously. This wire was used bare, four strands in parallel. No such trouble was found from viscous drag as with Heraeus platinum, and the results were considerably more satisfactory.

At atmospheric pressure the thermo-electric behavior of the two grades of platinum against lead is given by the following formulas.

Heraeus platinum:

$$E = (-3.092\,t - 0.01334\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (-3.092 - 0.02668\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = -0.02668(t + 273) \times 10^{-6} \text{ volts/°C}.$$

Baker's platinum:

$$E = (-1.788\,t - 0.0173\,t^2 + 0.000042\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (-1.788 - 0.0346\,t + 0.000126\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (-0.0346 - 0.000252\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

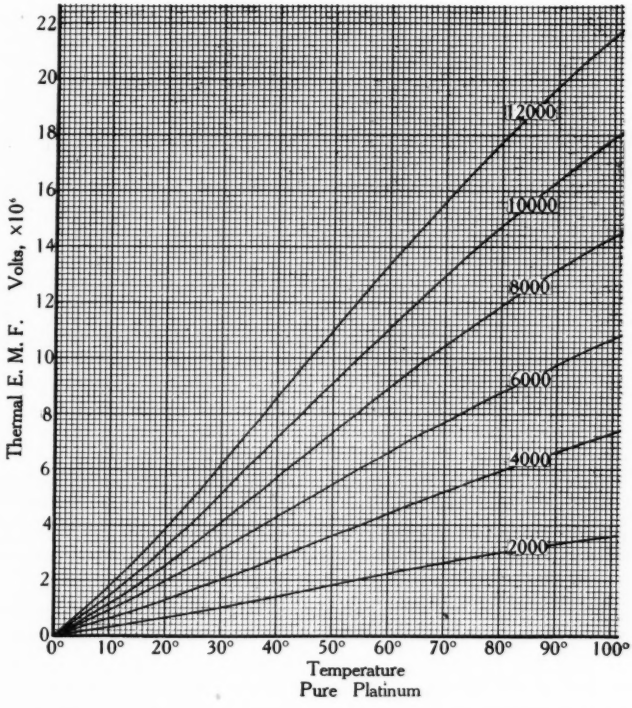

FIGURE 33. Heraeus Platinum. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm^2 indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

There are, therefore, considerable differences in the thermo-electric behavior. We would expect large differences in the behavior under pressure.

The pressure measurements on Heraeus platinum were made in an order the reverse of usual, beginning at 95° and ending at 25°. On the first application of seasoning pressure at room temperature the wire broke at 12000 kg. It was therefore evident that viscous

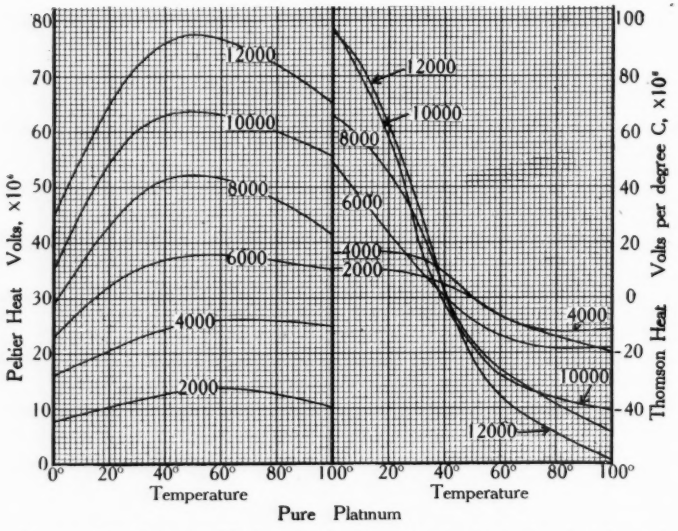

FIGURE 34. Heraeus Platinum. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

drag was going to be troublesome, and the reverse procedure was therefore adopted to insure getting as many readings as possible before rupture occurred. The four regular runs were successfully made, but at 75° the effect of drag was very large. After the four runs an attempt was made to repeat the run at 75°. Only three points were obtained, at 0, 4000, and 8000 kg., the wire breaking again at 12000. The points obtained lay about 3% lower than those of the

previous run at 75°, and in the direction necessary to make the points at 75° lie smoothly with those of other temperatures. The pressure runs on Baker's platinum were accomplished without incident. Two applications of 12000 were made at room temperature to season.

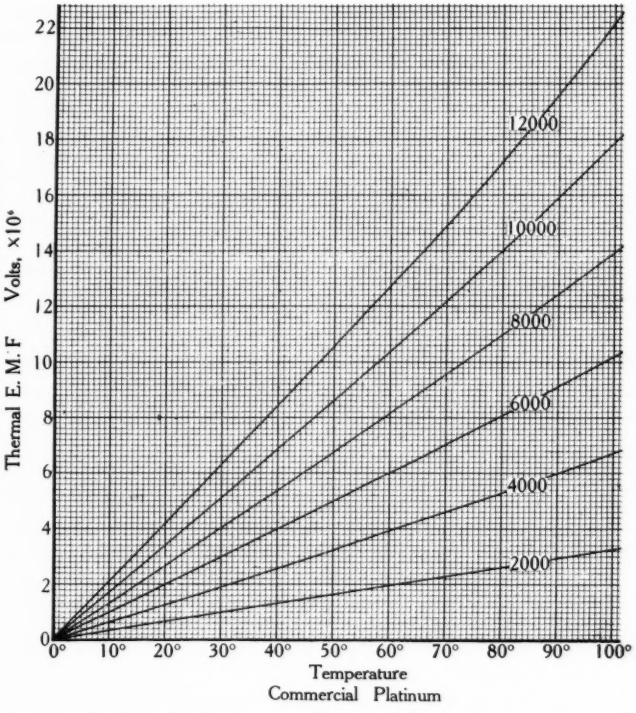

FIGURE 35. Baker's Platinum. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

Equilibrium was reached so rapidly as to suggest no shifting of internal equilibrium.

For the Heraeus platinum, the maximum departure of any single observed point from a smooth curve was 7.8% of the maximum

effect, except for the two bad points mentioned at 75°. The maximum zero correction was 2.5%, and the average numerical departure of all points from smooth curves was 0.81%. At constant temperature the relation between e.m.f. and pressure was linear. In passing to the curves at constant pressure from those at constant temperature it was necessary to disregard the 75° points, the discrepancy amounting to 4.3%, but the other points required no readjustment. If the second run at 75° could have been carried through, the adjustment

TABLE XXXII.

PLATINUM (PURE).

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+0.30	+.62	+.91	+1.18	+1.44	+1.79
20	.63	1.29	1.96	2.56	3.21	3.88
30	1.00	2.02	3.10	4.10	5.15	6.19
40	1.40	2.80	4.28	5.73	7.16	8.60
50	1.81	3.60	5.46	7.37	9.16	11.03
60	2.23	4.39	6.61	8.96	11.09	13.39
70	2.62	5.16	7.72	10.47	12.94	15.64
80	2.98	5.91	8.76	11.88	14.70	17.76
90	3.31	6.63	9.76	13.18	16.35	19.74
100	3.60	7.31	10.70	14.35	17.90	21.57

at 75° would have been only about 1%, so that there is reason to trust the results obtained.

For Baker's platinum, the maximum zero correction was 1.5% of the maximum effect, the maximum departure of any single observed point from a smooth curve was 3.1%, and the average numerical departure was 0.80%. At constant temperature the curves of e.m.f. against pressure are convex toward the pressure axis, not what one would expect, and the curves of e.m.f. at constant pressure against temperature are also convex toward the temperature axis. In passing from e.m.f. curves at constant temperature to those at constant pressure the maximum readjustment necessary was 1.1%.

TABLE XXXIII.

Platinum (Pure).

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+7.7	+16.1	+23.0	+29.0	+35.3	+44.8
20	10.3	20.5	32.2	43.0	54.5	64.8
40	12.8	24.7	37.0	51.4	62.9	76.0
60	13.7	26.0	37.6	51.7	63.0	76.6
80	12.7	25.7	36.6	47.5	59.9	72.3
100	10.1	25.0	35.1	41.4	55.6	64.9

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+10.9	+16.4	+49.2	+65.6	+97.0	+95.7
20	10.0	16.7	24.6	44.6	56.3	61.9
40	5.0	8.8	1.6	2.5	−2.2	2.5
60	−6.3	−6.7	−13.3	−26.0	−28.0	−36.0
80	−13.4	−12.0	−18.3	−38.8	−36.1	−48.6
100	−19.8	−11.2	−17.9	−48.9	−41.0	−59.0

The numerical results are shown in Tables XXXII, XXXIII and XXXIV and Figures 33, 34 and 35; only the e.m.f. is given for Baker's platinum. For both grades of platinum the e.m.f. is positive and rather large, increasing with pressure and temperature to 21.6×10^{-6} volts for the Heraeus platinum, and to 22.2 for Baker's at 12000 kg. and 100°. The similarity of these figures is somewhat unexpected in view of the difference in thermo-electric behavior at atmospheric pressure. The Peltier and Thomson heats are quite different, however. The Peltier heat of Heraeus platinum is positive, increasing

TABLE XXXIV.

PLATINUM (IMPURE).

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+.32	+.64	+1.01	+1.33	+1.70	+2.12
20	.65	1.28	2.01	2.67	3.41	4.23
30	.97	1.93	3.00	4.02	5.13	6.34
40	1.29	2.58	3.99	5.38	6.86	8.45
50	1.61	3.24	4.99	6.76	8.61	10.57
60	1.93	3.91	6.00	8.15	10.38	12.72
70	2.25	4.59	7.01	9.56	12.18	14.92
80	2.58	5.28	8.04	10.99	14.02	17.20
90	2.91	5.99	9.10	12.44	15.91	19.61
100	3.23	6.72	10.20	13.92	17.87	22.20

with pressure at constant temperature, but at each constant pressure passing through a maximum with rising temperature. The Peltier heat of Baker's platinum is also positive throughout, is somewhat larger than that of Heraeus platinum, and rises throughout with both temperature and pressure. The Thomson heat of Heraeus platinum changes sign, starting with positive values at low temperatures, and at each constant pressure becoming negative at higher temperatures. The Thomson heat of Baker's platinum rises to its highest positive values at the highest temperature, and for several pressures is negative at the lower end of the temperature range.

The value given by Wagner up to 300 kg. between 0° and 100° is $+18.6 \times 10^{-12}$ volts per degree per kg. The values found above by interpolation are 18.0 for the Heraeus, and 16.1 for Baker's platinum. The agreement with the purer specimen is as good as could be expected.

Molybdenum. This was a fresh piece, obtained through the kindness of Dr. W. D. Coolidge of the General Electric Company. The piece whose resistance under pressure had been measured was not

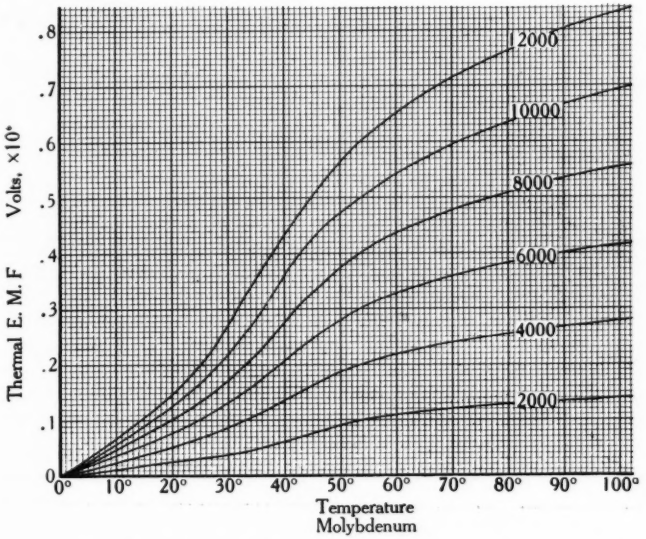

FIGURE 36. Molybdenum. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

large enough in diameter or long enough for use in this apparatus. The new piece was 0.008 inch in diameter, with a resistance of 0.54 ohms per ft. when cold. A piece 18 inches long, the piece to be exposed to pressure, was annealed by heating to a white heat with an electric current in an atmosphere of hydrogen. The hydrogen was not entirely free from oxygen, however, and there may have been some chemical effect. The outer connecting piece of wire was left

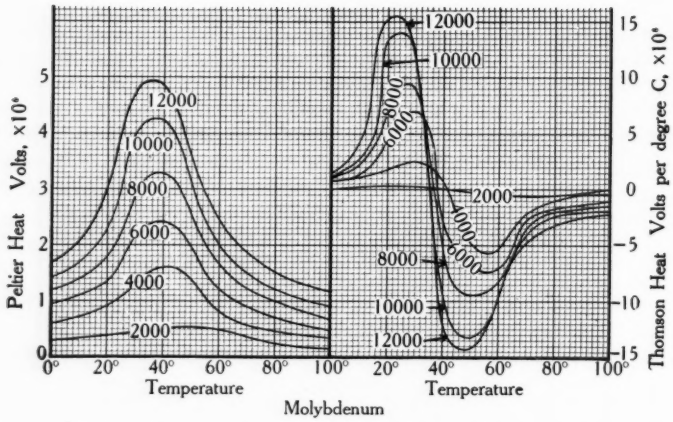

FIGURE 37. Molybdenum. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE XXXV.

MOLYBDENUM.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+.012	+.024	.037	.047	.057	.066
20	.025	.052	.078	.101	.124	.146
30	.039	.087	.133	.175	.219	.271
40	.065	.136	.209	.279	.357	.430
50	.093	.187	.282	.375	.472	.562
60	.109	.218	.328	.436	.543	.649
70	.121	.239	.359	.477	.594	.712
80	.129	.255	.383	.509	.634	.761
90	.135	.268	.401	.535	.666	.800
100	.140	.278	.415	.555	.693	.833

TABLE XXXVI.

MOLYBDENUM.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+.30	+.60	+.95	+1.20	+1.45	+1.69
20	.38	.91	1.35	1.79	2.28	2.93
40	.53	1.60	2.41	3.29	4.23	4.83
60	.47	.83	1.23	1.67	2.00	2.44
80	.25	.49	.74	1.02	1.23	1.52
100	.15	.33	.48	.67	.93	1.16

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	.0	+ .8	+ .8	+1.1	+ 1.2	+ 1.6
20	+ .6	+1.8	+4.4	+7.0	+13.2	+15.2
40	+ .3	+ .6	−2.5	−5.0	− 9.4	−11.6
60	−1.3	−5.3	−7.0	−8.0	− 9.3	− 9.7
80	−1.1	−1.1	−1.8	−2.1	− 2.5	− 3.2
100	+ .0	− .4	−1.1	−1.5	− 1.9	− 2.2

unannealed. This produced a large permanent zero reading, but should not introduce any error.

At atmospheric pressure the average temperature coefficient of resistance between 0° and 100° was found to be 0.00461; the relation between temperature and resistance was sensibly linear. This coefficient is considerably higher than that of the piece whose pressure coefficient was previously measured, for which the mean temperature coefficient was 0.00434. Both molybdenum and tungsten are known to vary considerably in properties with the amount of mechanical working, so that the difference between these two specimens may have been accountable for by the difference of size, and not by a difference of chemical constitution.

The thermo-electric behavior at atmospheric pressure against lead is given by the formulas:

$$E = (5.892\,t + 0.02167\,t^2 - 0.000025\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (5.892 + 0.04334\,t - 0.000075\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (0.04334 - 0.000150\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

For the pressure measurements the wire was seasoned by two applications of 12000 kg. at room temperature. The e.m.f. under pressure is small, reaching at the most at 12000 kg. and 100° only $+ 0.8 \times 10^{-6}$ volts. Individual readings showed large variations; the zero readings did not vary so much as those at high pressures. 32 readings in all were made; of these 6 were bad, showing variations from 7 to 50% of the total effect. The remaining 26 readings were not so bad, the maximum departure from a smooth curve being 5% of the total effect, and the average numerical departure 1.2%. It was not necessary to make any readjustment in passing from the e.m.f. curves at constant temperature to those at constant pressure.

The numerical results are shown in Tables XXXV and XXXVI and Figures 36 and 37. At constant temperature the relation between e.m.f. and pressure is linear; at constant pressure the curves against temperature pass through a point of inflection. This means a complicated behavior of both Peltier and Thomson heats. The Peltier heat is throughout positive, but at constant pressure passes through a pronounced maximum near 40°. The Thomson heat is both positive and negative, passing through pronounced positive maxima near 25°, and negative minima near 50°.

There are no previous results for comparison.

Tungsten. This, like molybdenum, was a fresh sample from Dr. W. D. Coolidge of the General Electric Company, the specimen

used previously for the resistance measurements not being large enough. This also was 0.008 inch in diameter. A piece long enough for both inside and outside pieces was annealed at one time by heating white hot with an electric current in an atmosphere of hydrogen under reduced pressure. The hydrogen was not pure, however, and there was appreciable formation of oxide. This treatment was successful in keeping the permanent zero reading down to a normal value.

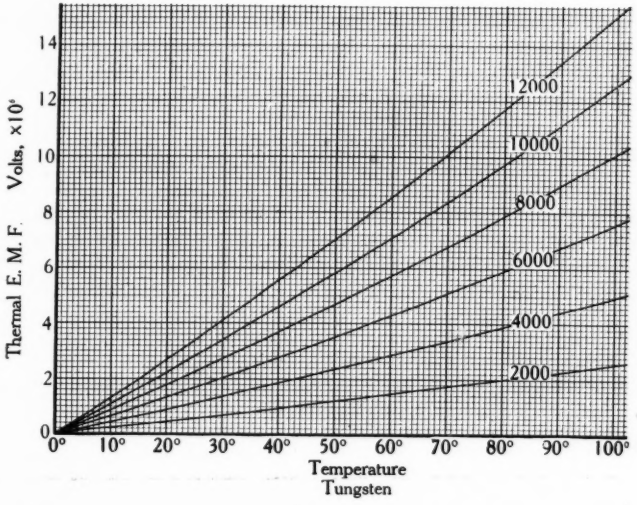

FIGURE 38. Tungsten. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

At atmospheric pressure the average temperature coefficient of resistance between 0° and 100° was 0.04317, the resistance being sensibly linear with temperature. The coefficient of the resistance specimen, which was only 0.0004 inch in diameter, was 0.00322. The considerable difference may again be due to the difference of mechanical treatment.

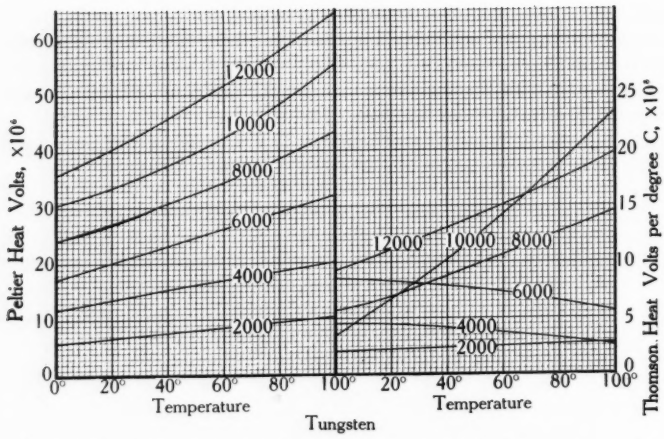

FIGURE 39. Tungsten. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE XXXVII.

TUNGSTEN.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+.22	+.44	+.65	+.89	+1.12	+1.33
20	.45	.90	1.33	1.80	2.26	2.70
30	.69	1.38	2.03	2.73	3.42	4.11
40	.94	1.87	2.76	3.69	4.61	5.56
50	1.19	2.36	3.52	4.69	5.84	7.05
60	1.45	2.87	4.30	5.72	7.10	8.58
70	1.71	3.39	5.00	6.78	8.40	10.15
80	1.98	3.92	5.92	7.86	9.75	11.76
90	2.25	4.45	6.75	8.97	11.15	13.42
100	2.53	4.99	7.60	10.12	12.61	15.14

TABLE XXXVIII.

TUNGSTEN.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+5.9	+11.7	+17.2	+24.1	+30.4	+35.7
20	6.7	13.6	20.1	27.2	33.5	40.5
40	7.7	15.5	23.1	30.7	37.5	45.9
60	8.7	17.1	27.1	34.4	42.3	51.8
80	9.5	18.6	29.0	38.6	48.3	58.0
100	10.4	20.3	32.0	43.4	55.4	64.8

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+2.0	+4.5	+8.5	+5.7	+3.5	+9.3
20	2.2	4.5	8.3	7.0	6.7	11.1
40	2.3	4.2	7.8	8.8	10.2	13.1
60	2.5	3.7	7.3	10.6	14.3	15.1
80	2.6	3.2	6.5	12.6	18.7	17.3
100	2.8	2.6	5.6	14.6	23.5	19.8

The thermo-electric behavior at atmospheric pressure against lead is given by the formulas:

$$E = (1.594\,t + 0.01705\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (1.594 + 0.0341\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = 0.0341(t + 273) \times 10^{-6} \text{ volts/°C}.$$

For the pressure measurements it was annealed once to 12000 kg. at room temperature. At 25°, 50°, and 75°, the readings under pressure went as smoothly as could be desired, but at 98° there was greater irregularity; here there was a permanent change of zero of 7% of the total effect. This was also the maximum departure of any point from a smooth curve. The average arithmetical departure of all points from smooth curves was 0.72%. In passing from curves of e.m.f. at constant temperature to those at constant pressure a maximum readjustment of 1% of the total effect was necessary.

The numerical results are shown in Tables XXXVII and XXXVIII and Figures 38 and 39. The effect is positive, increasing regularly with pressure and temperature, and is rather large, being 20 times as great as that of molybdenum. This was a surprise; the pressure coefficients of resistance of these two metals are nearly equal. The Peltier heat is positive, rising with pressure and temperature. The Thomson heat is positive, at the two extremes of the pressure range rising with temperature at constant pressure, but at intermediate pressures it falls with rising temperature.

There are no previous measurements for comparison.

Bismuth. This was electrolytic bismuth, prepared at the same time as the resistance specimen, but it was from the deposit on another electrode, so that the two specimens are not of necessity exactly alike. From the electrode deposit, the metal was made into wire by the same steps as the previous wire; the die through which this was extruded was 0.0285 inches in diameter, somewhat larger than the previous specimen. After extrusion, it was annealed by slow heating and cooling from room temperature to 100°, being maintained at 100° for 30 minutes. Much care was necessary in getting it in place in the pressure apparatus, but this was successfully accomplished without a single mishap.

At atmospheric pressure the average temperature coefficient of resistance between 0° and 100° of this specimen was 0.004372, which is somewhat lower than that of the previous specimen, 0.00441; the difference is no greater than has been formerly found to be due to differences of handling. The curve of resistance against temperature

at atmospheric pressure is strikingly convex toward the temperature axis, as was that of the other specimen. The two specimens are probably of equal purity.

The thermal electric behavior at atmospheric pressure against lead is given by the formulas:

$$E = (-74.42\,t + 0.0160\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (-74.42 + 0.0320\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = 0.0320(t + 273) \times 10^{-6} \text{ volts}/^\circ\text{C}.$$

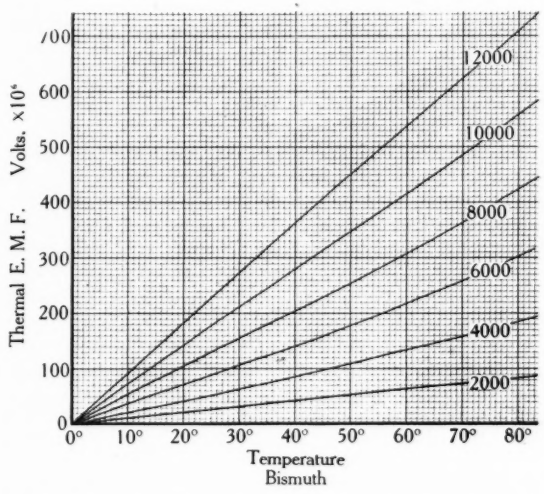

FIGURE 40. Bismuth. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

The pressure measurements of e.m.f. were satisfactory. The run at 25° was made without previous seasoning, in the desire to obtain all possible information before the confidently expected rupture, but this fear proved groundless, and the series of runs was completed without incident. Furthermore, it proved that seasoning was not necessary, the zero correction at 25° after the first application of 12000 kg. being only 0.16% of the maximum effect. Readings could be

easily made, there was no hysteresis or other evidence of incomplete internal equilibrium. The effect was so large that it was necessary to use the potentiometer direct connected. The maximum departure of any point from a smooth curve was 2.1% of the total effect, and the average numerical departure was 0.53%. As with the resistance specimen, the run at 100° was made impossible by breaking of the connection because of the low melting point of the alloy of bismuth with solder. In passing from curves at constant temperature to those at constant pressure no appreciable readjustment was necessary.

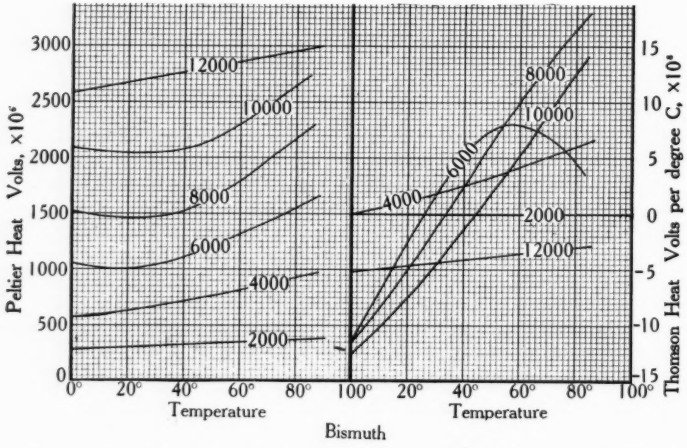

FIGURE 41. Bismuth. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal, to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

The numerical results are shown in Tables XXXIX and XL and Figures 40 and 41. The e.m.f. is positive and very large, increasing regularly with pressure and temperature to 710×10^{-6} volts at 100° and 12000 kg. The largest effect found for any other metal was for thallium, which gave only 52.5. Except for the largeness of the value, the only unusual feature is the upward curvature of the e.m.f. curves at constant temperature plotted against pressure; this denotes a greater proportional effect for the same pressure increment at the

higher pressures. The Peltier heat is positive; in general it increases with rising pressure and temperature, but at the middle of the range it passes through a flat minimum with rising temperature. The Thomson heat shows complicated behavior; at 2000 kg. it is throughout zero, at 4000 it is negative, and at higher pressures it is initially negative, rising to positive values.

Wagner found at 300 kg. between 0° and 100° the value 707×10^{-12}

TABLE XXXIX.

BISMUTH.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+11.	+21.	+38.	+54.	74.	93.
20	21.	42.	73.	106.	145.	185.
30	32.	64.	107.	156.	214.	275.
40	42.	87.	141.	205.	281.	364.
50	53.	110.	177.	255.	348.	452.
60	64.	134.	218.	308.	416.	539.
70	74.	159.	259.	365.	487.	625.
80	85.	185.	302.	425.	560.	710.

volts per degree per kg. The value indicated by interpolation and extrapolation of the data above is 531×10^{-12}. The agreement is not good. In view of the great differences found in the previous work in the electrical properties of bismuth of different origins, and the large effect of minute impurities, it would have been most desirable if Wagner had allowed some estimate of the purity of his sample by stating its temperature coefficient at atmospheric pressure.

TABLE XL.

BISMUTH.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	+289.	+574.	+1070.	+1530.	+2080.	+2580.
20	311.	644.	1030.	1490.	2050.	2670.
40	332.	720.	1090.	1530.	2070.	2760.
60	353.	800.	1330.	1790.	2300.	2860.
80	374.	950.	1550.	2180.	2650.	2960.

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
0°	0	0	+1150.	−1150.	−1250.	−520.
20	0	+117.	− 290.	− 500.	− 760.	−470.
40	0	250.	+ 500.	+ 250.	− 160.	−440.
60	0	430.	+ 800.	+1000.	+ 530.	−370.
80	0	600.	+ 460.	+1660.	+1270.	−280.

Constantan. This was obtained from the Electrical Alloys Co. of Morristown, N. J., and is sold by them under the trade name "Ideal." The chemical analysis given by them is: Copper 55%, Nickel 44%, Manganese 1%, and Iron 1.4%. The diameter of the wire was 0.010 inches. There is of course not a great deal of interest at the present stage of affairs in the behavior of a substance so complicated; the study of alloys as such would begin with simpler ones. This alloy is used extensively in electrical measurements, however, and there is some practical interest in its behavior. I have not previously given data for any of the electrical properties of this substance; the list here given is composed of (1) the temperature coefficient of resistance at atmospheric pressure, (2) thermal e.m.f. at atmospheric pressure against lead, (3) pressure coefficient of resistance, (4) pressure effect on thermo-electric quality.

At atmospheric pressure the resistance passes through a maximum with rising temperature near 12°. The values found for the resistance were as follows: at 0°, 1.0000; at 25°, 1.0000; at 50°, 0.9998; at 76° 0.9994, and at 97°, 0.9989. The change is, therefore, as slight as that of manganin for any small range, but the minimum of manganin is more pronounced than the maximum of this, so that the total change between 0° and 100° of "Ideal" is greater than of manganin.

The thermo-electric behavior at atmospheric pressure against lead is given by the formulas:

$$E = (-34.76\,t - 0.0397\,t^2) \times 10^{-6} \text{ volts},$$
$$P = (-34.76 - 0.0794\,t)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = -0.0794(t + 273) \times 10^{-6} \text{ volts/°C}.$$

Its thermal e.m.f. against commercial copper is represented by

$$E = -(38.50\,t + 0.0445\,t^2) \times 10^{-6} \text{ volts}.$$

This may be compared with results of Johnston and Adams [13] for wire from the same source. They give their results in the form of a table; the maximum discrepancy between their results and that above is at 100°, where they give 4227×10^{-6} volts against 4295 above. The difference is not greater than one would expect in different specimens with different handling.

The pressure coefficient of resistance was measured by the method described in the previous paper. The wire was wound bare on a

13 J. Johnston and L. H. Adams, Amer. Jour. Sci. **31**, 510, 1911.

bone core. It had been previously seasoned by alternately heating to 140° for 30 minutes, and slowly cooling to room temperature for 15 minutes, repeating three times. For the pressure measurements it was seasoned by a single application of 12000 at room temperature. After this first application of pressure there was a permanent decrease of resistance amounting to 0.03% of the total resistance. The effect of pressure is to increase the resistance very slightly, instead of to decrease it, as for pure metals. Measurements were made at three temperatures; 0°, 50°, and 97°. Within these limits the coefficient

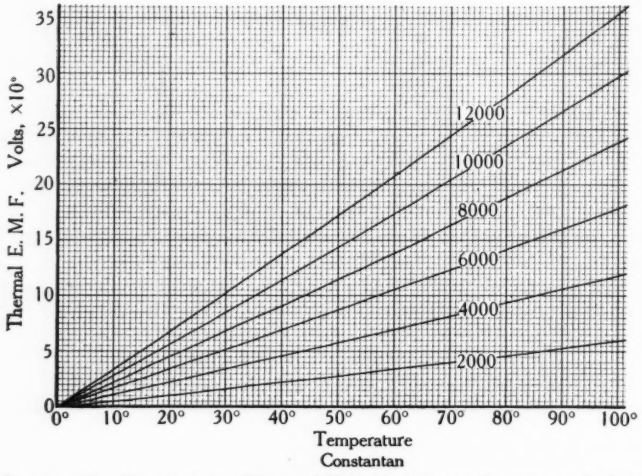

FIGURE 42. Constantan. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other being at the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

is independent of temperature, and the relation between pressure and resistance is linear up to 12000 kg. The pressure coefficient between 0° and 100° up to 12000 kg. was found to be $+0.0_{6}409$, pressure measured in kg./cm.². The smallest coefficient found in the previous work for a pure metal was that of tungsten, which was $-0.0_{6}125$.

In contrast to the very small effect of pressure on resistance is its very large effect on thermo-electric quality. The effect is positive,

as it is for the majority of metals, and is exceeded in value only by bismuth and thallium. The wire was seasoned for the pressure runs on thermal e.m.f. by raising pressure to 11300 kg. at room temperature, then raising temperature to 100° for $2\frac{1}{2}$ hours, the pressure rising to 11500. Large permanent zero readings might be expected with this substance, because its thermal e.m.f. against iron is so high, but its homogeneity was so great that the zero effect was only about 5% of the pressure effect at any temperature. A curious effect was

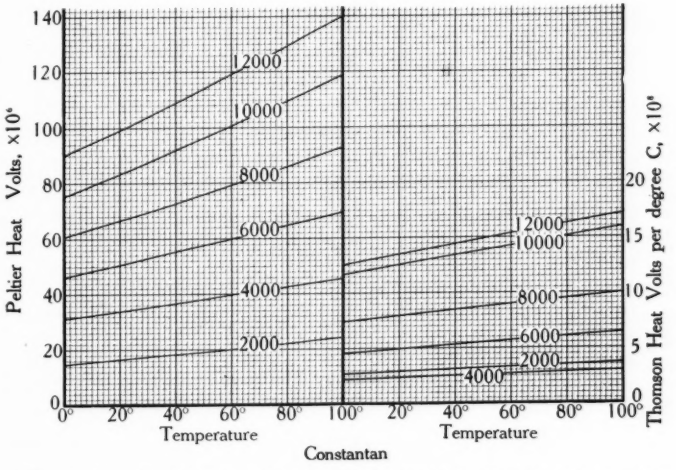

FIGURE 43. Constantan. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

observed immediately after changes of pressure, before temperature equilibrium was reached; there were violent oscillations of e.m.f., changing sign with a period of a few seconds, which gradually disappeared. This is possibly an effect of shifting internal equilibrium connected with the complicated nature of the alloy, but is more probably a pure temperature effect, and is particularly prominent here because of the unusually large e.m.f. between constantan and the steel of the cylinders. The immediate effect after a change of pres-

sure is a difference of a difference, the residual effect being the difference between the e.m.f's. at the hot and cold ends brought about by the difference of temperature produced by compression between the inside and the outside of the cylinder. When one considers that the instantaneous rise of temperature by compression might be 10°, it does not seem surprising that there should be such oscillations with a galvanometer sensitive enough to be thrown off the scale by 6×10^{-6} volts. The e.m.f. between iron and constantan is 50×10^{-6} volts per degree.

Because of the complications involved in any interpretation of the

TABLE XLI.

CONSTANTAN.

Thermo-electromotive Force, volts $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
10°	+0.55	+1.14	+1.71	+2.25	+2.78	+3.35
20	1.11	2.29	3.44	4.53	5.60	6.75
30	1.68	3.45	5.18	6.84	8.47	10.19
40	2.26	4.62	6.94	9.17	11.38	13.67
50	2.85	5.80	8.72	11.53	14.34	17.20
60	3.45	6.99	10.51	13.82	17.34	20.77
70	4.06	8.18	12.32	16.36	20.38	24.38
80	4.68	9.38	14.14	18.81	23.46	28.03
90	5.31	10.59	15.98	21.29	26.58	3.73
100	5.95	11.81	17.84	23.79	29.74	35.47

instantaneous effects, I gave up the attempt to observe them after a few metals had been measured. The effects may change sign with the same metal with pressure and temperature. I did not happen to make observations like those on constantan with any other substance except manganin, also an alloy. This is probably only a coincidence.

The pressure measurements of e.m.f. went fairly smoothly. Except for two points at 96° with discrepancies of 4.0 and 2.3%, the maximum departure of any point from a smooth curve was 1.3% and the average numerical departure was 0.26% of the total effect. The

TABLE XLII.

CONSTANTAN.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+15.	+31.	+46.	+61.	+75.	+90.
20	17.	34.	51.	67.	83.	99.
40	18.	37.	55.	73.	92.	109.
60	20.	40.	60.	79.	105.	119.
80	22.	43.	65.	86.	109.	130.
100	24.	46.	70.	93.	119.	140.

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+2.7	+2.2	+4.6	+7.4	+11.7	+12.6
20	2.9	2.3	5.0	7.9	12.6	13.5
40	3.1	2.5	5.3	8.4	13.4	14.4
60	3.3	2.7	5.7	9.0	14.3	15.3
80	3.5	2.8	6.0	9.5	15.2	16.2
100	3.7	3.0	6.4	10.1	16.0	17.2

maximum zero correction was 1.1%. In passing from the curves of e.m.f. at constant temperature to those at constant pressure the maximum readjustment was 0.60%.

The numerical results are shown in Tables XLI and XLII and Figures 42 and 43. The effect is positive, rising regularly with pressure and temperature to 35.5×10^{-6} volts at 100° and 12000 kg. At constant temperature the relation between e.m.f. and pressure is linear. The Peltier heat is positive, rising with pressure and temperature. The Thomson heat is also positive, and rises with pressure and temperature; at every constant pressure it is directly proportional to the absolute temperature.

Constantan, of unstated composition, was one of the substances measured by Wagner. He gives to 300 kg. and between 0° and 100° 31.1 and 26.4×10^{-12} volts per degree per kg. for two different specimens. The value given by interpolation of the data above is 29.7, falling within Wagner's limits.

Manganin. This was from the same spools as the coils used in measuring resistance, and is of German origin, probably nearly 20 years old. The resistance at atmospheric pressure shows a maximum near 30°. The following values of resistance were found: at 0°, 1.0000; at 26°, 1.0007; at 50°, 1.0006; at 76°, 1.0002; and at 97°, 0.9995.

The thermo-electric behavior at atmospheric pressure against lead is given by the formulas:

$$E = (1.366\,t + 0.000414\,t^2 + 0.0000112\,t^3) \times 10^{-6} \text{ volts},$$
$$P = (1.366 + 0.00828\,t + 0.0000336\,t^2)\,(t + 273) \times 10^{-6} \text{ volts},$$
$$\sigma = (0.00828 + 0.0000672\,t)\,(t + 273) \times 10^{-6} \text{ volts/°C}.$$

The resistance of this wire was also measured because I now had apparatus for getting more accurately the variation with temperature of the pressure coefficient than formerly. Previously I had measured the same coil successively at different temperatures against an absolute gauge, and found only a small variation in the pressure coefficient up to 80°. The change may be slightly different for different specimens, even from the same spool. This procedure was now improved upon by simultaneously measuring two coils, both exposed to the same pressure, but placed in different pressure cylinders and maintained at different temperatures with two different thermostats. The one coil, that with which pressure was measured, was always maintained at the same temperature, 40°, whereas the temperature of the other coil was varied for different runs. The new coil was

seasoned by baking at 140° for several hours, and by several applications of 12000 at room temperature. After this seasoning there was no appreciable change of resistance after a run under pressure. At 0° and 25° the pressure coefficient of resistance is practically the same; as it is also at 50°, 75° and 100°, but between 25° and 50° there was an increase of coefficient of 0.7%. However, the measurements were not as good as they might be, and the isolated change between 25° and 50° is probably not real.

The e.m.f. measurements under pressure were made in the regular

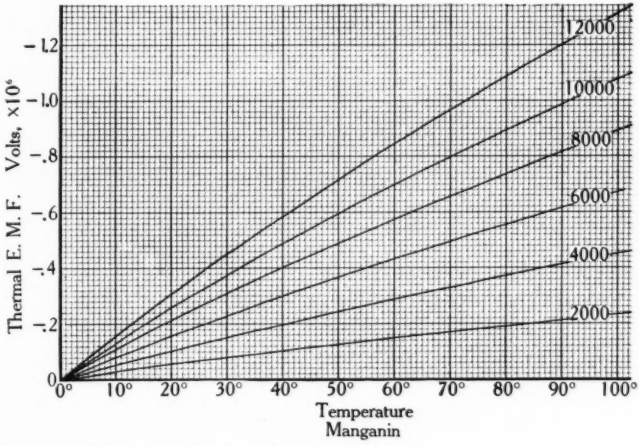

FIGURE 44. Manganin. Thermal E.M.F. of a couple composed of one branch of uncompressed metal, the other compressed to the pressure in kg./cm.² indicated on the curves, the junctions being at 0°C and the temperature plotted as abscissae.

way. The effect is small and negative. The wire was seasoned for the e.m.f. measurements by baking to 140° at atmospheric pressure, and by one application of 12000 kg. at room temperature. The measurements at the lower temperatures were regular, but at the higher temperatures the irregularities increase very rapidly. This is as one would expect in an alloy. The greatest discrepancy was shown by the final zero point at 97° which lies off a smooth curve by 18% of the maximum effect at 97°; at this temperature the average arithmetic departure is 7.7%; at 75° the maximum departure is at 8000

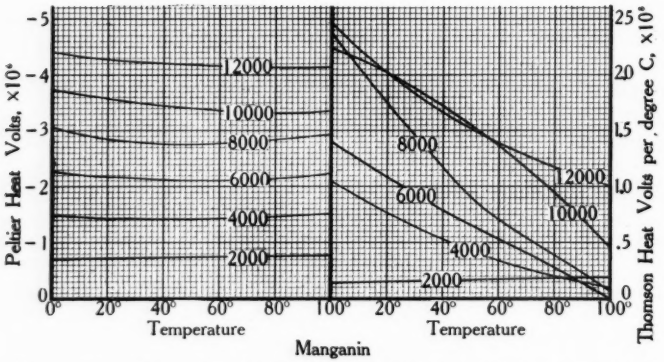

FIGURE 45. Manganin. On the left, the heat absorbed by unit quantity of electricity in flowing from uncompressed metal to metal compressed to the pressure indicated on the curves, as a function of temperature. On the right, the excess of Thomson heat in metal compressed to the pressure indicated on the curves over uncompressed metal, as a function of temperature.

TABLE XLIII.

MANGANIN.

Thermo-electromotive Force, volts × 10^6.

Temp. C degrees	Pressure, kg./cm.² 2000	4000	6000	8000	10000	12000
10°	+.026	−.053	−.081	−.111	−.133	−.158
20	.057	.103	.157	.215	.258	.308
30	.076	.151	.230	.311	.377	.451
40	.100	.197	.300	.402	.490	.588
50	.123	.242	.367	.489	.597	.719
60	.146	.286	.431	.573	.700	.846
70	.168	.329	.493	.655	.799	.968
80	.190	.371	.554	.736	.895	1.087
90	.211	.412	.614	.816	.988	1.202
100	.232	.452	.673	.894	1.079	1.314

TABLE XLIV.

MANGANIN.

Peltier heat, between uncompressed and compressed metal, Joules per conlomb $\times 10^6$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	−.71	−1.50	−2.27	−3.07	−3.74	−4.41
20	.73	1.44	2.20	2.90	3.56	4.28
40	.74	1.44	2.13	2.77	3.45	4.20
60	.75	1.43	2.12	2.77	3.36	4.15
80	.76	1.47	2.14	2.83	3.32	4.13
100	.77	1.51	2.24	2.94	3.35	4.14

Thomson heat, excess in compressed over uncompressed metal, Joules per conlomb per °C $\times 10^8$.

Temp. C degrees	Pressure, kg./cm.²					
	2000	4000	6000	8000	10000	12000
0°	+.14	+1.04	+1.40	+2.38	+2.24	+2.46
20	.15	.77	1.08	1.75	2.02	2.01
40	.16	.53	.78	1.17	1.72	1.66
60	.17	.34	.53	.70	1.36	1.39
80	.18	.25	.28	.39	.95	1.17
100	.19	.10	.00	.07	.46	1.01

kg. and is 3.8% of the maximum effect at 75°, while the average departure is 2.4%; at 50° the maximum departure is 2.8% of the maximum effect at 50° and the arithmetical average is 1.07%; and at 25° the maximum departure is 3% of the maximum effect at 25°, and the average departure 0.6%. Within these limits of error the relation between e.m.f. and pressure at constant temperature is linear. In passing from curves of e.m.f. at constant temperature to those at constant pressure the maximum readjustment was at 97°, as was to be expected; here it was 12% of the maximum effect. No appreciable readjustment was necessary at the lower temperatures. The following data are to be expected, therefore, to have considerably greater relative accuracy at the lower part of the temperature range.

The numerical results are shown in Tables XLIII and XLIV and Figures 44 and 45. The effect is negative, increasing regularly with pressure and temperature to -1.31×10^{-6} at 12000 kg. and 100°. The effect is among the smallest found. It is interesting to compare the small effect of pressure on the resistance of constantan and its large effect on thermal e.m.f. with precisely the reverse behavior here. The Peltier heat is negative, increasing with pressure, but at each constant pressure it is nearly independent of temperature. The Thomson heat, on the other hand is positive, at the lower pressures changing but little, but at the higher pressures falling with rising temperature.

Wagner gives between 0° and 100° and to 300 kg. -8.5×10^{-12} volts per degree per kg. The value given by interpolation of the data above is -11.6×10^{-12}. The agreement is perhaps as close as could be expected in an alloy from presumably different sources.

Effect of Tension on Thermo-Electric Quality.

The general method of measurement is the same as that employed in measuring the effect of hydrostatic pressure on thermo-electric quality, namely to measure the thermal e.m.f. of a couple composed of two branches of the same metal, one of which is under tension, and the other of which is free. The connections are shown schematically in Figure 46. A length of the wire to be measured is doubled on itself, running from A to E to C. At E it is fastened to a heavy block capable of withstanding any load that is to be applied to the wire. At A and C the ends of the wire are fastened to the under sides of the left and right hand pans respectively of two equal arm balances,

indicated in the figure by the arrows AB and CD, by means of which a load may be applied to either wire separately or together. The upper and lower ends of the wires are surrounded by two thermostated baths, indicated by the open rectangles in the figure, which may be kept at any desired two different temperatures. In use the lower bath was always packed with ice, and the upper bath was set at any desired temperature between 0° and 100° C. The two wires

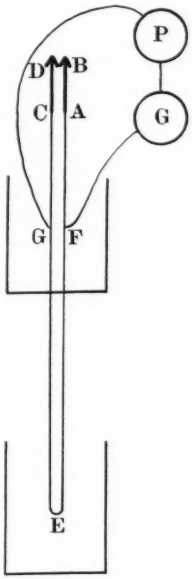

FIGURE 46. Scheme of connections used in finding effect of tension on thermo-electric quality.

are tapped at the middle of the upper bath by two flexible leads of copper connecting to the galvanometer G and the potentiometer P. These instruments were the same as were used in the previous measurements. The balances are insolated from each other, so that the circuit runs from G to P to G to F to E to G. If the two wires are precisely alike, there is no thermal e.m.f. in this circuit for any difference of temperature between GF and E, but if one of the wires is

loaded, the material of the two branches of the couple now becomes effectively different, and a thermal e.m.f. appears. This was measured as a function of tension and temperature difference.

Various precautions were taken in performing the experiment which need not be gone into here at length. The two wires passed through a heavy glass tube for their entire length, and in this way were protected from contact with the water of the bath. To secure temperature equality and diminish error from heat conduction along the wires from one bath to the other, the glass tube was filled, up to the level of the water in the upper bath, with Bureau of Standards resistance oil. As a further precaution against slight variations in temperature, the glass tube was covered for the entire length of immersion in the upper bath with a compound tube of $\frac{1}{4}$ inch thick copper on the inside fitting closely into an outer iron tube also $\frac{1}{4}$ inch thick. Since the lower bath was always filled with ice and consequently was not exposed to slight oscillations of temperature, such a precaution was not necessary below. The approximate dimensions were; depth of each bath 1 ft., free distance between baths 2 ft., diameter of glass tubing 1 inch.

It has been already stated that the results of these experiments were very irregular, the effect varying with the nature of the specimen. In the following the nature of the results will be briefly indicated; each result given is the mean of determinations on the right and the left hand wires.

Nickel. Wire from the same manufacturers but from a different spool from the pressure sample was used. This was 0.005 inches in diameter. A maximum tension of 2000 kg./cm.^{2} was applied. The results were fairly good; the two samples agreed on the average within about 5%. The thermal e.m.f. may be represented by the following equations:

$$\begin{aligned}
&\text{At } 31^\circ \quad \text{e.m.f.} = (.00335T - 0.0_660T^2) \times 10^{-6} \text{ volts},\\
&\text{at } 51^\circ \qquad\quad = (.00577T - 0.0_5132T^2) \times 10^{-6},\\
&\text{at } 77.5^\circ \qquad\quad = (.0081\ T - 0.0_5175T^2) \times 10^{-6},\\
&\text{at } 94.5^\circ \qquad\quad = (0121\ T - 0.0_537T^2) \times 10^{-6}.
\end{aligned}$$

In these formulas T is the tension in kg./cm.^{2} The direction of the e.m.f. is from unstretched to stretched at the hot junction. Paying attention only to the change of volume, this would correspond to a pressure effect of from compressed to uncompressed at the hot junction This is of the opposite sign from the observed pure pressure effect.

Copper. This was commercial wire of 0.020 inches diameter.

The maximum tension applied was 700 kg./cm.^{2} Within this range the e.m.f. was linear with tension. Trustworthy measurements were obtained only at 95°. Here the two specimens differed from the mean by 20%.

$$\text{e.m.f.} = 0.00056T \times 10^{-6} \text{ volts.}$$

The direction of e.m.f. is from unstretched to stretched at the hot junction. This corresponds to from compressed to uncompressed at the hot junction, and is opposite in sign from the pure pressure effect.

Iron. This was annealed "ingot" iron, from the same piece of metal as that of the pressure measurements. Its diameter was 0.025 inches, and it was subjected to a maximum tension of 500 kg./cm.^{2} Satisfactory readings were obtained at two temperatures; the two wires differed by less than 10%. The results are covered by the formulas:

$$\begin{aligned} \text{At } 52° \quad \text{e.m.f.} &= (0.0120T - 0.0_4235T^2) \times 10^{-6} \text{ volts,} \\ \text{at } 95° \quad &= (0.0223T - 0.0_442T^2) \times 10^{-6}. \end{aligned}$$

The effect has a pronounced maximum near the middle of the tension range; this recalls the complicated behavior under hydrostatic pressure, although the range of tension is comparatively much lower than the range of pressure. The e.m.f. is from unstretched to stretched at the hot junction, corresponding to from compressed to uncompressed. This corresponds to the sign of the pure pressure effect over the first portion of the pressure range.

Aluminum. Commercial stock of 0.0195 inches diameter was used. Satisfactory results were obtained at two temperatures; the two wires differing by about 10% from the mean. The results are given by the formulas:

$$\begin{aligned} \text{At } 50.5° \quad \text{e.m.f.} &= (0.0088T - 0.0_567T^2) \times 10^{-6} \text{ volts,} \\ \text{at } 76° \quad &= (0.0088T - 0.0_547T^2) \times 10^{-6}. \end{aligned}$$

The departure from linearity, contrary to what one might expect, is only slight. The abnormal behavior under pressure, however, is reflected in the slight change of e.m.f. with temperature. The direction of e.m.f. is from unstretched to stretched at the hot junction, corresponding to from compressed to uncompressed. This corresponds to the initial direction of the pressure effect.

Brass. This was commercial wire of 0.008 inches diameter. The

tension range was high, 2800 kg./cm.^{2} Under the most unfavorable conditions the two wires differed 50% from the mean. The results are given by the formulas:

$$\begin{aligned} \text{At } 52^\circ \quad \text{e.m.f.} &= (0.00022T - 0.0_73T^2) \times 10^{-6} \text{ volts}, \\ \text{at } 77^\circ \quad &= (0.00013T - 0.0_712T^2) \times 10^{-6}, \\ \text{at } 94^\circ \quad &= (0.00047T - 0.0_75T^2) \times 10^{-6}. \end{aligned}$$

At 52° the departure from linearity is so great that the e.m.f. passes through a maximum. This disappears at the higher temperatures. E.m.f. is from stretched to unstretched at the hot junction, corresponding to from uncompressed to compressed for the pure pressure effect. This is the first example met of an effect of this sign. The pure pressure effect was not measured.

Manganin. This was from the same stock as the pressure sample, but not from the same piece. The range of tension was 1300 kg./cm.^{2} The two samples, contiguous lengths, did not give the same sign for the effect. The one showing the smaller effect reversed in sign with changing temperature, at the lower temperatures being opposite in sign from the more active piece, but at 98° becoming of the same sign, although only 10% of it. The effect for the more active specimen was not linear, but is less proportionally at the higher temperatures, and at 32° actually passes through a flat maximum near $\frac{3}{4}$ of the maximum tension. The maximum values of e.m.f. for this piece were: 0.1, 0.25, 0.38, and 1.33×10^{-6} volts at 32°, 50°, 75°, and 95° respectively. The direction is from unstretched to stretched at the hot junction, corresponding to a pressure effect from compressed to uncompressed. This agrees with the pure pressure effect.

Dependence of Thomson Heat on Temperature Gradient.

Although it is not directly connected with the immediate object of this work, I nevertheless made experimental examination of one other point, both because I was in a position to make the experiment with comparatively little effort, and because this point is indirectly involved as an assumption made in deriving the formulas used in deducing the Peltier and the Thomson heats from the total e.m.f. The assumption is always made that the Thomson heat depends only on the temperature at a point, and not on the temperature gradient, that is, on the rate of flow of heat. The existence of such a dependence on gradients would mean the possibility of the existence of thermoelectric currents in unequally heated circuits of a single homogeneous

metal. This effect was often looked for in the early days of the subject, and the concensus of opinion was that the effect does not exist; whenever an effect like it was obtained, it was always explainable by imperfect homogeneity in the metal. At the same time there seems to be no reason why the effect might not exist, and it occurred to me that with present apparatus we are in a position to push the limits within which the effect must lie much further than before. The circuit on which I experimented consisted of liquid mercury, and was therefore completely homogeneous. The mercury was contained in a quartz capillary; at the center of the circuit the capillary was drawn down with thin walls to perhaps 0.5 mm. diameter and 0.25 mm. thickness of wall. Over the neck in the capillary was slipped a piece of tightly fitting mica. A simple arrangement allowed a jet of water to be directed against the quartz on one side of the mica and on the other side a small gas flame. In the mercury underneath the mica there was, therefore, an intense temperature gradient. The two ends of the quartz capillary were led to an ice bath, and from this connection made through copper leads to a galvanometer. There was therefore no chance for thermo-electric action unless there were one due to the temperature gradient. The galvanometer was a very sensitive Thomson galvanometer constructed by Coblentz; I owe the opportunity to use it to the kindness of Dr. I. Gardner. With this I could establish that there was no e.m.f. in the mercury of as much as 3×10^{-11} volts, up to temperature gradients steep enough to vaporize the mercury at one end of the constriction in the capillary. Care had to be taken in establishing this result; for example, if the part of the circuit containing the gradient is not horizontal, an effect will be found due to the effect of pressure differences on thermo-electric quality.

The effect, if it exists, is therefore exceedingly minute. The equations above show that if the effect exists consequences with regard to other effects are involved. We have the equation

$$\frac{d}{dt}\left(\frac{P_{AB}}{t}\right) + \frac{1}{t}(\sigma_A - \sigma_B) = 0$$

Hence if σ_A for example, depends on the temperature gradient, then P_{AB} must also, or the Peltier heat would depend on the total quantity of heat flowing into the junction. Such an effect has not been observed, and therefore inferentially the Thomson heat is independent of temperature gradient. However, the observations on Peltier heat have presumably been no more accurate than those on the freedom of total e.m.f. from effects of gradient.

General Survey of Results.

The first impression given by the measurements under pressure is of bewildering and perhaps hopeless complexity, but there are nevertheless certain uniformities and normal types of behavior. Let us for the first discussion disregard detail and take as a measure of the effects the maximum e.m.f., Peltier heat, and Thomson heat listed in the tables above. The normal effect of pressure on e.m.f. is positive; there are only three out of 20 cases, manganin, Mg, and Co, in which the effect is persistently negative to the highest pressures and temperatures; and for only three other metals, Fe, Al, and Sn is the effect negative over any part of the range. The range of values of maximum e.m.f. is from $+710 \times 10^{-6}$ volts for Bi to -20.6×10^{-6} for Co. Similarly, the normal pressure effect on Peltier heat is positive, that is, heat is absorbed by the positive current in flowing from uncompressed to compressed metal. There are only four cases of negative Peltier heat under pressure, manganin, Sn, Mg, and Co. The range of values is from 2960×10^{-6} for Bi to -90.5×10^{-6} for Co. The Thomson heat under pressure is also normally positive, Co, Fe, and Bi being the only negative cases. The range of values is from 220×10^{-8} for Zn to -280×10^{-8} for Bi.

When, however, we try to correlate the thermo-electric behavior with other electrical properties of the metals we find complete lack of connection. In table XLV the metals are arranged in a number of columns, in each column the order being the order of relative magnitude of the property standing at the head of the column. In the first place, the pressure effect on e.m.f. is not greatest for the most compressible metals, as we might expect, but the effect is apparently quite independent of the compressibility. Compare, for example, the positions of Pb and Mg in the compressibility column with their positions in the pressure e.m.f. column. It was pointed out in a previous paper that the effect of pressure on resistance is approximately proportional to its effect on volume; this is shown in the table by the similarity of the columns of compressibility and pressure effect on resistance. There is accordingly very little connection between the pressure effect on resistance and that on e.m.f. The conclusion suggests itself that there is little connection between the mechanism which determines the thermo-electric behavior of a metal and its electrical conductivity. This is further borne out by the lack of parallelism between the columns of pressure effect on resistance with those of pressure effect on Thomson and Peltier heat.

There is almost exact parallelism between the columns of pressure effect on e.m.f. and on Peltier heat; these two columns differ only by two single inversions, Al with Cu, and manganin with Sn. This of course means that nearly all the total e.m.f. in a pressure thermo-

TABLE XLV.

THE METALS IN ORDER OF DECREASING NUMERICAL MAGNITUDES OF VARIOUS PROPERTIES.

The horizontal bars in some columns show where the effect changes sign.

Specific Resistance	Temp. Coeff. of Resis. 0°–100° at 0 kg.	Thomson heat at 0° and 0 kg.	Peltier heat against Pb at 0° and 0 kg.	Pressure effect on resistance	Pressure effect on E.M.F.	Pressure effect on Peltier heat	Pressure effect on Thomson heat
Bi	Fe	Cd	Fe	Pb	Bi	Bi	Zn
Cons.	Tl	Mo	Cd	Tl	Zn	Zn	Pt
Man.	Ni	W	Mo	Sn	Tl	Tl	Cd
Pb	Sn	Bi	Zn	Cd	Cd	Cd	Tl
Tl	Bi	Cu	Au	Mg	Cons.	Cons.	Sn
Fe	Al	Au	Cu	Zn	Pd	Pd	Pb
Ni	Mo	Ag	Ag	Al	Pt	Pt	Al
Sn	Cu	Man.	Tl	Ag	W	W	W
Pt	Cd	Al	W	Au	Ni	Ni	Cons.
Pd	Pb	Mg	Man.	Fe	Ag	Ag	Ni
Co	Zn	Pb	Sn	Pd	Fe	Fe	Mo
Cd	Ag	Sn	Pb	Pt	Pb	Pb	Ag
Zn	Au	Tl	Mg	Cu	Au	Au	Pd
W	Mg	Zn	Al	Ni	Cu	Al	Au
Mg	Pt	Fe	Pt	Mo	Al	Cu	Cu
Mo	Co	Pt	Pd	W	Mo	Mo	Man.
Al	W	Pd	Co	Co	Sn	Man.	Mg
Au	Pd	Ni	Ni	Cons.	Man.	Sn	Co
Cu	Cons.	Co	Cons.	Man.	Mg	Mg	Fe
Ag	Man.	Cons.	Bi	Bi	Co	Co.	Bi

electric couple (that is, a couple of two branches of the same metal, one compressed and the other not) is provided by the difference of Peltier heat at the hot and cold junctions, and comparatively little by the pressure effect on the Thomson heat. This has been otherwise

obvious from the fact that the relation between e.m.f. and temperature at constant pressure has been in most cases approximately linear.

The columns of pressure effect on Peltier heat and Thomson heat are not obviously related. Most striking is the transposition of Bi from the head of one column to the bottom of the other; the pressure effect on Peltier heat of Bi is the maximum positive, and on the Thomson heat the maximum negative. One draws the conclusion that the

TABLE XLVI.

RATION OF MAXIMUM CHANGE OF THOMSON HEAT WITHIN THE RANGE 0°–100° C AND 0 TO 12000 KG./CM.^{2} TO THOMSON HEAT AT 0°C AND 0 KG.

Sn	− .81
Tl	− .108
Cd	+ .0105
Pb	∞
Zn	− .81
Mg	0
Al	+4.5
Ag	+ .041
Au	+ .0295
Cu	+ .0285
Ni	− .017
Co	+ .013
Fe	+ .40
Pd	− .0098
Pt	−0.131
Mo	+ .013
W	+ .021
Bi	− .32
Cons.	− .0079
Man.	+ .011

Thomson heat mechanism and the Peltier heat mechanism are not intimately related. The pressure effect on Thomson heat inclines to show parallelism to the pressure effect on resistance.

The thermo-electric behavior at atmospheric pressure (Peltier heat against lead and Thomson heat) also shows little direct connection with the pressure effects. There is no obvious connection between other pairs of columns; the thermo-electric mechanism seems to stand in a class by itself.

The magnitude of the change in the Thomson heat produced by pressure compared with the total Thomson heat under atmospheric conditions is of interest. The relative effect of pressure on the properties of most solids is comparatively small; for example, the maximum effect found before on resistance was 14% for lead, and the effect on volume is only a few per cent. We should expect a similar state of affairs with the Thomson heat. This is true, except for the anomalous metals. The total pressure effects with Al, Bi, Fe, Sn, and Zn, are all of the order of magnitude of the whole effect at atmospheric conditions, but the other metals show the smallness of the effect to be expected. The results are shown in Table XLVI.

So far, we have considered the effects only in broad outline, but when we come to consider the detailed variations with pressure and temperature we find great complexity. The normal behavior of e.m.f. is a regular rise with pressure and temperature; the slope of the e.m.f. curves at constant pressure increasing with rising temperature, but the slope at constant temperature decreasing with rising pressure. Fe, Al, and Sn are examples of complicated variations of e.m.f. with pressure and temperature, and we have also met other examples where the slope at constant pressure may decrease with rising temperature, or the slope at constant temperature may increase with rising pressure. As for the detail of variation of Peltier heat or Thomson heat with pressure and temperature, so many different types are presented that it is useless to try to enumerate them.

The Entropy of Electricity.

By an extension of a remark made by Professor E. H. Hall with regard to the ordinary thermo-electric diagram, we may find a function giving the entropy of the electricity in the metal as a function of pressure and temperature.

A couple composed of two branches of the same metal, one at 0 pressure, the other at pressure p, running between 0° and t° has a definite e.m.f., E. E is a function of p and t. If we add to E (p,t) $E_{pb}(t)$, that is, the e.m.f. against lead at atmospheric pressure, we shall obtain a function ξ (p,t) such that $t\left(\frac{\partial^2 \xi}{\partial t^2}\right)_p$ is the Thomson heat at any pressure and temperature and $t\left(\frac{\partial^2 \xi}{\partial t \partial p}\right)$ is the Peltier heat.

That is $$\left(\frac{\partial Q}{\partial t}\right)_p = t\left(\frac{\partial^2 \xi}{\partial t^2}\right)_p,$$

and $$\left(\frac{\partial Q}{\partial p}\right)_t = t\,\frac{\partial^2 \xi}{\partial p \partial t}.$$

It is obvious that $\left(\frac{\partial \xi}{\partial t}\right)_p$ is equal to the entropy of one coulomb of electricity, because $dQ = tdS$,

and

$$\left(\frac{\partial Q}{\partial t}\right)_p = t\left(\frac{\partial s}{\partial t}\right)_p = t\left[\frac{\partial}{\partial t}\left(\frac{\partial \xi}{\partial t}\right)_p\right]_p \text{, and } \left(\frac{\partial Q}{\partial p}\right)_t = t\left(\frac{\partial s}{\partial p}\right)_t = t\left[\frac{\partial}{\partial p}\left(\frac{\partial \xi}{\partial t}\right)_p\right]_t.$$

If we had some means of determining the work done on electricity as well as the entropy we would be in a position to completely determine its behavior.

This function ξ gives at once the means of finding on the p, t plane the slope of the lines of constant entropy. I have made this computation for all the metals listed above. As is to be expected, the line assumes every possible slope. It thus appears that there is no simple relation between the ordinary thermodynamic properties of a metal and the thermodynamic properties of the electricity in the metal.

Conclusion and Summary.

In this paper measurements are given of the thermal e.m.f. of couples composed of two branches of the same metal, one of the branches being under uniform hydrostatic pressure and the other branch at atmospheric pressure, the junctions between the branches being at 0°C and some other variable temperature. The range of the work covers 20 pure metals and 2 alloys, and all pressures up to 12000 kg./cm.^{2} and all temperatures between 0° and 100°. From these measurements of e.m.f. the Peltier heats and the Thomson heats may be deduced by the ordinary thermodynamic reasoning as a function of pressure and temperature. By the Peltier heat of the couples measured in this work is meant the heat absorbed by unit quantity of electricity in flowing across the junction from uncompressed to compressed metal, and by the Thomson heat of the couple is meant the excess of heat absorbed by unit quantity of electricity in flowing through one degree temperature difference in the compressed metal over the uncompressed metal. With regard to these heats, my position

in this paper has been that the ordinary thermodynamic argument, by which the formulas have been deduced, allows conclusions only as to the quantities of heat, and that no conclusion is justified as to the local e.m.f's. corresponding to these heats. Complete diagrams and tables are given for the e.m.f., Peltier, and Thomson heats of these couples.

The nature of the results was unexpectedly complicated. The normal state of affairs is apparently a positive effect of pressure on both Peltier and Thomson heats, but there are numerous examples of negative effects, and almost none of the metals show regular variation of these quantities with pressure and temperature within the range. Three metals, tin, iron, and aluminum, show complicated variations of the e.m.f. of the couple, there being maxima and minima with both pressure and temperature within the range.

The effect of tension on thermo-electric quality of a few of the 20 metals was measured, and the results again were complicated. In general the pure volume effect on thermo-electric quality is different, according as the change of volume is brought about by a hydrostatic pressure or a tension. This is the reverse of the behavior of electrical resistance, which is determined primarily by the change of volume, regardless of whether it is produced by tension or hydrostatic pressure.

As a bye-product, the dependence of Thomson heat on temperature gradient has been measured for mercury, and the possibility of such an effect of gradient has been made more remote than before.

The unexpected complications found makes these results disappointingly meagre in their suggestions as to the nature of the thermo-electric mechanism. The conclusions are mostly negative in character. The most unmistakable inferences may be drawn as to the untenability of the old gas-free-electron theory of metals, but this is not now new enough to be worth the experimental trouble. This conclusion was drawn 10 years ago by Wagner from his data up to 300 kg., and the results of this paper can add nothing to the conclusions of Wagner in this regard, since our results are in essential agreement over our common range. Further than this, the results suggest most strongly that the thermo-electric mechanism must be comparatively complicated, that it cannot be at all of the simplicity imagined by the free electron theory and that most likely the effects which we measure are the resultant of different effects, which some times, at least, work in opposite directions. What these effects may be, we are not in a position at present to speculate.

In the projected paper mentioned in the introduction on general

considerations on thermo-electric action, it will be pointed out that the data of this paper allow certain information to be gathered about the behavior of various constants of thermionic emission under pressure. The latent heat of vaporization of electrons, the density of the electron atmosphere, and the Volta contact force between an uncompressed and a compressed metal may be determined as a function of both pressure and temperature, except for an undetermined function of pressure alone.

Finally, it may not be too daring to say that it seems to me that much of my previous work on high pressure effects at least suggests a direction in which we may look for the explanation of these complicated effects. The thermodynamic properties of liquids under high pressures and all the mutual relations of the polymorphic forms of solids have been found to be quite as complicated under pressure as the thermo-electric properties above. I have shown in detail that probably the properties of both liquids and solids are to be explained in terms of the same agency, the effect of the characteristic shape of the atoms, or, if one prefers to express it so, the nature of the field of force surrounding the atom. It seems most probable that the electrons in passing from atom to atom, or in playing about between the atoms, may be subjected to forces changing in a complicated way as the atoms are forced by pressure into positions of varying degrees of adaptation to each others irregularities.

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